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N.N. ZININ

(1812-1880)

IN MEMORY OF N. N. ZININ-FOUNDER OF THE RUSSIAN SCHOOL OF ORGANIC CHEMISTS*

(On the 75th. Anniversary of his Death)

S. N. Danilov

"The name of Zinin will always be revered by those who hold the achievements and greatness of Russian science near and dear to the heart" [1].

A. M. Butlerov

Seventy-five years ago, on February 6/18**1880, in St. Petersburg, died the eminent chemist Nikolai Nikolaevich Zinin (1812-1880), whose works in the field of organic chemistry brought great glory to the chemical science in Russia. N. N. Zinin- a remarkable scientist, discovered new directions in the synthesis of organic compounds, highly fruitful for both science and industry. In him was consolidated, among contemporaries both in Russia and abroad, the glory of outstanding scientist, widely cultured and authoritative professor, brilliant lecturer and distinguished public servant during the 40-70's of the previous century. The scientific-pedagogical activity of Nikolai Nikolaevich Zinin left a deep mark in the development of world science and in the instruction of chemistry in our higher schools.

One of his older students, A. M. Butlerov, creator of the chemical structure theory, wrote [1] about his teacher: "The origin of the Russian chemical school is associated with his scientific and pedagogical activities; Russian chemistry is almost exclusively indebted to him for its assumption of an independent existence; his works were the first to cause the scientists of Western Europe to place Russian chemistry in a respected position. The renowned name of Zinin reveals itself in a whole series of Russian chemists' names, made famous in science, and the debt of these chemists as students of Zinin, or as students of his students, is great. Russian science can well be proud of the name of Zinin".

A contemporary of Zinin, A. A. Voskresensky [2] (1809-1880), also made a major contribution to the development of Russian chemistry in the early part of the 19th century, both as the result of his scientific, and especially, his pedagogical activity. Included among his students are D. I. Mendeleev, N. N. Sokolov, N. A. Menshutkin, and others. Included in the number of eminent chemists, direct students of Zinin, we will name, other than A. M. Buterlov, also N. N. Beketov, A. P. Borodin, L. N. Shishkov, A. P. Engelhardt, and A. A. Zagumenny.

N. N. Zinin and A. A. Voskresensky completed their first studies in the 30's of the previous century in Germany in the Giessen laboratory, working under the direction of the famous German chemist J. von Liebig (1803-1873), who studied in the 20's, together with his friend F. Wöhler, in France in Gay-Lussac's laboratory. A. M. Butlerov and D. I. Mendeleev – leaders in chemical science – in contrast to their teachers, began their scientific activity in their own country.

In recognition of the important role played by N. N. Zinin and A. A. Voskresensky in the development of Russian chemistry, and as a tribute to their outstanding scientific achievements, the Russian Physical-Chemical Society established in 1880 (the year when both of these eminent chemists died) the Zinin and Voskresensky prizes for stimulating further chemical advances in Russia [3]. From their scientific studies, chemical instruction and preparation of chemists,appeared the basis on which the glorious Russian schools of chemical science arose, and which created

* The expanded speech "Life and Scientific Activity of N. N. Zinin" was given by S. N. Danilov at the solemn assembly held February 18,1955 in the S. M. Kirov Military-Medical Acedemy, dedicated to the 75th. anniversary of the death of the great scientist and organizer of the Leningrad Section of the D. I. Mendeleev All-Union Chemical Society and the S. M. Kirov Military-Medical Acedemy.

** Old/reformed Russian calendar. [Translator].

favorable conditions for the ingenious contributions made by their students A. M. Butlerov and D. I. Mendeleev – the chemical structure theory and the periodic table of chemical elements.

1. Outline of the Life and Activity of N. N. Zinin

The life, scientific, pedagogical and public activities of Zinin have been described in the most glowing terms by his students A. M. Butlerov and A. P. Borodin [1], and later also by other authors [4,5].

Zinin was born on August 13/ 25, 1812 in one of the formerly outlying Russian regions in Transcaucasia, in the town of Shusha, in what is now the Azerbaijan SSR, close to the Armenian SSR. After successful instruction and graduation from the Saratov gymnasium Zinin was enrolled in 1830 as a student at Kazan University in the Mathematical Section of the then Philosophical Faculty, where he studied mathematics, atronomy, physics, chemistry and the natural sciences.

The teachers [1] of Zininnoted a wide scientific interest in their pupil. Even in his gymnasium years he showed a great desire to study nature. Gold medals were bestowed on him when he went from the 2nd course ("discharge") to the 3rd, at the time being the last, and also when he graduated from the university. The second medal and the Candidate of Science degree were obtained by him [1] for his treatise in the field of astronomy: "The Perturbations of Elliptic Planetary Motion". Enrolled in 1833, after graduation from the university, as a junior physics instructor he soon began to teach analytical mechanics, hydrostatics and hydraulics, and somewhat later also astronomy, and also conducted scientific investigation in the field of magnetism (with Prof. I. M. Simonov).

From 1835 Zinin became committed to the teaching of chemistry. At the time in contrast to the following 40's, 50's and 60's, the scientific faculty at Kazan University failed to have any outstanding representatives. In 1835 Zinin passed his magister's examinations and in October, 1836 he defended his dissertation on the topic: "The Phenomena of Chemical Affinity and the Superiority of Berzelius' Theory of Constant Chemical Proportions Over the Chemical Statics Theory of de Berthollet", for which he was granted the learned (higher) degree of Magister of Natural Sciences. In 1837 Zinin was assigned to spend 2 years abroad (later the assignment was extended another year) for scientific purposes and to become familiar with the teaching of chemistry, physics and chemical technology.

Zinin began his scientific endeavors abroad in Berlin, where he attended the chemical lectures given by the notables of the time – Mitscherlich and Rose, and at the same time he became interested in biology and medicine. The great fame of the laboratory and scientific school of Justus von Liebig attracted Zinin to Giessen. The greater part of his assignment was spent in completing, at the request of von Liebig, his investigation of the transformations of benzaldehyde into benzoin and of benzil into benzilic acid. Here he succeeded in finding a fruitful method for the preparation of benzoin from benzaldehyde by catalytic treatment with potassium cyanide and in elucidating the origin of this keto alcohol in crude almond oil, obtained from the amygdalin found in almonds.

Zinin spent some time (in 1840) in Paris in Pelouse's laboratory, where at the time the first investigations on nitrocellulose were being made, which, possibly, attracted the attention of Zinin to nitric acid derivatives.

Returning to Russia in the fall in 1840, Zinin passed his doctoral examinations at St. Petersburg University and on January 30, 1841 he defended his doctor's dissertation, which was based on the experimental work that he had done in the laboratory of Justus von Liebig. He returned to Kazan University in the spring of the same year and was confirmed as Professor Extraordinary of the Chair of Chemical Technology, since the occupation of the Chair of Chemistry had already been awarded to K. K. Klaus, known for his studies on the metals of the platinum group and the discovery of the new element – ruthenium.

In these, as in all of the remaining years of his life, Zinin was seriously interested in chemical technology problems, while continuing work in the field of synthetic organic chemistry. Some of his papers were of an applied nature, as, for example, the production of aniline dyestuffs [6]; he was largely responsible for the introduction of nitroglycerin in practice. The Swedish inventor A. Nobel, in his preparation of dynamite and smokeless ballistite powder, made use of the researches of Zinin and his co-workers.

About this time the construction of a new chemical laboratory at Kazan University was completed [5], and here both Zinin and Klaus conducted their dintinguished researches, the first in the field of organic chemistry, and the second in the field of inorganic chemistry. A. M. Butlerov calls both of these chemists his tutors [1].

The salutary influence exerted by Zinin on his young pupils is expressed by Butlerov [1] in the following words: "The inspiring influence, arousing scientific enthusiasm, shown by my former teacher is valued by all of those who were fortunate enough, the same as myself, to start their practical acquaintance with science under his beloved guidance".

During the years 1842-1845 Zinin published the extremely important experimental data obtained by him on the reduction of nitrobenzene and other aromatic nitro compounds to amines (the Zinin reaction). These original and revolutionary studies of Zinin immediately attracted great attention both in Russia and abroad.

Butlerov [1] in his reminiscences has the following to say with respect to some of these studies made by Zinin: "A sixteen-year old student at the time, I was naturally intrigued by the external side of the chemical phenomena, and was especially taken with the handsome red plates of azobenzene, the yellow needle crystals of azoxybenzene and the glistening silvery scales of benzidine".

In 1847 Zinin was invited to come to St. Petersburg as Professor of the Medical-Surgical Academy, where he worked from 1848 to 1874, showing a great scientific, pedagogical,and public activity.

Due to the lack of suitable laboratory facilities at the Medical-Surgical Academy, Zinin at first had to pursue his scientific studies in his home laboratory. Toward the end of the 50's and in the early 60's, with very close participation by Zinin, a large chemical laboratory was built at the Medical-Surgical Academy, existing even now as the S. M. Kirov Military-Medical Academy. Zinin also devoted much effort to the construction of a new chemical laboratory at the Russian Academy of Sciences, in which laboratory he started to do experimental work beginning with 1867.

In 1855 Zinin was elected as an Assistant in the Russian Academy of Sciences, and then in 1858 followed his election as Extra-ordinary Academician, and in 1865 as Ordinary Academician. In 1873 the French Academy of Sciences elected him as a Correspondent Member.

In addition to his extensive activities [1] in the Medical-Surgical Academy and in the Russian Academy of Sciences, Zinin fulfilled various duties and continued to do experimental work in chemistry. But not only the Medical-Surgical Academy and Russian Academy of Sciences benefited by Zinin's work: he participated in many state institutions and commissions, made scientific-technical expeditions to the Crimea, to Caucasus (1852) and to Ural (1866), sat at the Paris Exposition as a Member of the Jury (1867), etc.

Also to be mentioned is the prominent part that was played by Zinin in the organization and in the activities of the Russian Chemical, later the Physical-Chemical Society. From 1868 to 1878 he was President of this Society. At the World Industrial Exposition in London held in 1876 the Russian Chemical Society organized a large chemical products section, containing mostly organic compounds, of which many were personally synthesized by Zinin and his students.

In recognition of his great scientific services and as a token of gratitude for his warm participation in the welfare of the society the Russian Physical-Chemical Society bestowed the title of Honorary Member on Zinin in 1878. The London and German Chemical Societies also paid tribute to Zinin and gave him the same title of Honorary Member in their respective societies.

A. P. Borodin writes in his memoirs [1]: "Profound patriot, deeply and intelligently loving Russia, understanding and taking to heart her interests, N. N., by his attitude, was foremost in zealously guarding the autonomy of Russian science and the intellectual development of the Russian individual"

N. N. Zinin died of a kidney ailment in his 68th year on February 6/ 18,1880.

On his death A. M. Butlerov wrote [1]: "Russian chemistry was associated in extremely close blood relationship with its eminent deceased representative, and the irretrievable loss is felt with heavy pain"

At the German Chemical Society meeting held on March 8, 1880 the German chemist A. W. Hofmann [7] arose and delivered a speech dedicated to the memory of Zinin, in which he characterized in glowing words the significance of the deceased scientist's works; "Today", Hofmann began his speech, "I must communicate to this assembly the death of one of the older illustrious chemists, an individual who exerted a remarkable and enduring influence on the development of organic chemistry. From the letter of Butlerov as President of their Society we have learned of the death of N. N. Zinin in St. Petersburg".

Hofmann concluded his speech with the words: "If Zinin had done nothing more than convert nitrobenzene into aniline, then still his name would have remained inscribed in gold letters in the histroy of chemistry".

2. Theoretical Opinions of Zinin

An examination of the scientific wealth left by Zinin reveals that the ideas expressed in his studies were new for the times, ideas which were experimentally confirmed by him. Placing himself in the first years of his scientific

activity with the adherents of the theory of radicals as propounded by von Liebig and Wöhler, he quickly grasped the great significance of the newly-born theories of substitution and types, and gave a very clear example of such reactions on the basis of his discovered reaction process for the reduction of nitro compounds to amines. The replacement of two oxygen atoms by two hydrogen atoms was a more impressive, although also a more complicated example of substitution and simultaneous reduction than was the substitution (metalepsis) of the hydrogen atoms in acetic acid by chlorine. The discovery of the benzoyl radical (von Liebig and Wöhler, of the chloroacetic acids (Dumas), and the reduction of nitro compounds to amines (Zinin), shook the very foundations of the Berzelius electrochemical theory. These discoveries showed that radicals should be assigned more than just the hydrocarbon composition, or their carbon, hydrogen and nitrogen composition, and that they should be regarded as being a fixed component part of organic molecules.

During the years that Zinin spent in von Liebig's laboratory there was a lively discussion on the merits of the theory of radicals and the electrochemical theory of Berzelius. In his paper [8] appearing in 1839: "Some Current Organic Chemistry Problems", Berzelius mentions the great advances that had been made in this division of chemistry in the past 10-12 years, discusses the question of radicals, assigning a binary nature to organic substances, and considers oxygen-containing substances as being the oxides of complex radicals, despite the conclusions derived from the studies of von Liebig and Wöhler on the benzoyl radical, on uric acid, and on multi-basic acids.

In the same place [8] von Liebig expressed his objections to the chemical formulas and understanding of radicals as interpreted by Berzelius. In the same year [9] Dumas published his treatise on the chloroacetic acids and on the constitution of organic compounds as being in accord with the substitution theory, which theory was rejected [8] by Berzelius in a letter to Wöhler. Von Liebig, having made rebuttal to Berzelius' viewpoint by raising the question of whether there would be a change in compound type in the chlorination of acetic acid, joined forces [10] with Dumas, believing that the formula presented by Berzelius for benzaldehyde and benzoyl chloride, $C_{14}H_{10}O_6 + 2C_{14}H_{10}O_3$ was incorrect.

Somwhat later Dumas [9] again published a paper on the tenets of the substitution theory and the theory of types, to which von Liebig made rebuttal [10], while Wöhler (under the pseudonym of S. C. H. Windler) published a derogatory pamphlet against these theories [11].

In his doctoral dissertation (1841) Zinin [12] gives his opinions on the theoretical questions discussed in the literature. He shows that the benzoyl radical is a complex radical, present in a number of compounds; the hydrocarbon compound (analog) of this radical (in oil of bitter almonds) corresponds to the series that are substituted by chlorine, iodine, bromine, cyano, sulfur, "amide", etc.; the benzoyl radical "passes from one compound to another, just like a simple body", by the double decomposition rule.

With respect to the opinion held by Dumas of the benzoyl radical being the oxide of either the hydrocarbon radical $C_{14}H_{10}$ or C_7H_5, Zinin states in his dissertation that this in no way changes the conclusion made by von Liebig and Wöhler with respect to the benzoyl radical. As regards the formulas assigned by Dumas to benzoic aldehyde $C_{14}H_{10}O_6 + 2C_{14}H_{10}O_3$ and to benzoic acid $C_{14}H_{10}O_3$, where $C_{14}H_{10}$ is acknowledged as a radical, which, as it were, forms with 6 hydrogen atoms a peculiar "ammonia-like base $-C_{14}H_{10}O_6$," then Zinin considers them as being artificial.

From his deliberations on the reactions discovered by Mitscherlich for the formation of: 1) benzene ("gasoline" $C_{12}H_{12}$) in the distillation of labdanic (benzoic) acid with excess aqueous lime, 2) sulfobenzene, and 3) nitrobenzene, which served Mitscherlich as a basis to acknowledge the presence of the "benzide" (phenyl, $C_{12}H_{10}$ radical in both these compounds and in benzoic acid, Zinin came to the following conclusion: the Mitscherlich theory deserves special consideration, since it is "well-nigh the first experiment on the theoretical elucidation of a number of phenomena appearing in organic chemistry", but that these explanations are not applicable to the benzoyl group of compounds.

According to Mitscherlich, "benzoylhydrogen will be the compound of benzene (gasoline) with carbon monoxide", which Zinin considers unacceptable. He directly states in this dissertation that the theories of radicals and types "easily and satisfactorily explain the origin and properties of many bodies".

Toward the end of the 40's N. N. Zinin joined in with the viewpoints of Gerhardt and Laurent.

A. M. Butlerov, visiting his teacher in St. Petersburg in 1853-1854, states that Zinin at the time was the center about which the scientific youth collected, and that he urgently recommended that Butlerov be guided by the teachings of Laurent and Gerhardt in both science and in instruction and pointed out the significance of the diverse char-

acter possessed by hydrogen in organic compounds. On the subject of his discussions with Zinin, Butlerov has the following to say in his memoirs: "The short discussions I had with N. N. during this stay in St. Petersburg were sufficient to make the time stand out as epochal in my scientific education".

Zinin in the beginning of his paper (1854) on copulated ("coupled") ureas ("ureides") points [13] to the great importance possessed by substitution phenomena, and also the fact that the same element in complex bodies can be present in different states.

Three different element states can be distinguished: metaleptic, where one element can take the place of another; copulated ("coupled"), where one element can extract another similar element from the complex compound, emerging together with it; and the basic state, which is known for the hydrogen atom and where its replacement by a metal can occur. All three states are inherent to hydrogen: metaleptic hydrogen, bound to carbon, coupled hydrogen, i. e. typical hydrogen, and basic (metallic) hydrogen, found in acids, whereas only the metaleptic and coupled states are inherent to chlorine, oxygen and sulfur.

N. N. Beketov, a student of Zinin and later an Academician, in his magistral dissertation (1853) [14], in speaking of Gerhardt remarks that the French scientist failed to give the deserved attention to the chemical significance of the reacting (operating) elements, and that the hydrogen, linked to carbon atoms, possesses different properties from the hydrogen atoms that are linked to amphid and haloid bodies. Later, N. N. Sokolov (1859) in his doctoral dissertation [15] writes that ". . . . . in organic compounds there are not only two types of hydrogen: metaleptic and metallic, but many different types of hydrogen in the chemical sense"; he gave a correct evaluation of the properties of the hydrogen atoms found in the alcoholic hydroxyl and in the carboxyl group of lactic acid.

In these statements of Zinin, Beketov, and Sokolov, can be seen the beginnings of the idea of the reciprocal influence of atoms in molecules, which was briefly mentioned by Gerhardt [16], and which was formulated by Butlerov, who stated that the atoms found in molecules, even when not directly connected, exert a mutual influence on each other.

The chemical structure theory was constantly associated in the studies of Butlerov [17] with the idea of mutual atomic influence. This idea of mutual atomic influence received great attention in the studies of V. V. Markovnikov [18] and developed into a science, becoming the basis for electronic representations in organic chemistry.

In his works (doctoral dissertation, lectures and papers) Zinin touches on some extremely general chemical problems. He rejects [12] the viewpoint of Berzelius on catalytic phenomena as being the result of the operation of a special catalytic force; he divides the phenomena, ascribed to this nonexistent force, into two classes: 1) bodies combine and decompose either by themselves without any apparent reason under the influence of external factors or only when in contact with certain bodies, in which connection the latter fail to be changed; 2) in order to effect reaction the decomposition process should be accomplished in the unchanged body itself.

In the lectures of Zinin [19] beginning in the 50's we find a definite denial of the existence of a vital force: "Constantly the mystics assume the existence of a special vital force in our bodies. . . ." Speaking of the delusions under which the alchemists suffered and of the faith in the miraculous, Zinin had the following to say: " A wise man was Bacon, who said: 'why do you seek laws for nature in the mind; instead seek laws for the mind in nature'."

In the beginning of one of his speeches (1847) Zinin [20] states that ". . . . a new branch of knowledge has developed and requires its own laws in order that organic chemistry can be called an independent science", which has its own problems and which, in addition, is used ". . . . . directly to solve the problems that are offered by other natural sciences". Speaking that chemistry had made great strides and that "striving for the miraculous and the impossible has finally ceased to be the general lot of science", and that " . . . . . the highest task of science consists in the seeking of the relationships that exist between composition and properties – a composition law, and together with that a law for the origin of bodies", the orator dwells in detail on the importance of organic substances and of exchange reactions in the growth of plants and animals.

The basic conclusion derived from the facts and phenomena that were examined in the speech is: "Nearly all of the phenomena that we observe are accomplished under the influence of chemical laws, and as soon as the question relates to this domain of science, its answer will always be definite and exact".

3. Experimental Works

The synthesis studies made by Zinin are the pride of not only Russian, but also of world-wide science. Each paper is the start of new directions in synthetic organic chemistry and the source of a large number of investigations in all lands even up to now. Special attention is devoted to the action of reducing agents and in part of oxidizing

agents on organic substances (synthesis of benzil from benzoin), replacement of oxygen atoms by hydrogen atoms (in nitro compounds under the conditions of the famous Zinin reaction for the preparation of amines), and also the reduction of hydroxyl (synthesis of desoxybenzoin from benzoin) and aldehyde groups (synthesis of hydrobenzoin). Becoming interested in substitution and coupling reactions, he developed a synthesis for the simpler ureides.

Despite the great diversity of the chemical compounds and reactions with which Zinin was occupied, all of his works were bound by one direction and community of ideas. He was interested in the chemical phenomena occuring during fermentation and decay, and also in the hydrolytic cleavage of both amygdalin from almonds to benzoic aldehyde, and of the substances from mustard to mustard oil. These problems relative to fermentation and catalytic phenomena are discussed in the first pages of his doctoral dissertation. To him belongs the laboratory synthesis of mustard oil and many researches on benzoic aldehyde derivatives.

The first reaction discovered by Zinin, the benzoin condensation of benzaldehyde under the influence of potassium cyanide, can serve as an example of the simultaneous oxidation-reduction reactions [21], possessing such great significance in alcoholic and other fermentations.

His reaction for the synthesis of amines from nitro compounds proved to exert an exclusively great influence on the development of the chemistry of aromatic compounds and the industry of organic dyestuffs.

Zinin Reaction — The Reduction of Nitro Compounds. In the first paper [22] in which he describes the preparation of new organic bases, Zinin indicated (reported March 18, 1842) that he wanted to elucidate the properties of the compounds that are obtained in the treatment of nitro compounds with hydrogen sulfide. In his work on the synthesis of benzoin from benzaldehyde (1840) he mentions his attempts to reduce benzil with sodium sulfide. Zinin returned to the compounds, obtained in the treatment with nitric acid ". . . to the hydrocarbons, where the hydrogen equivalents are replaced by an equal number of hyponitric acid equivalents", i. e. to the nitro compounds.

The present nitro group was then regarded as being the hyponitric acid NO_4, where the total oxygen affinity is equal to 8. The radical NO_4 or "copula" of nitric acid was derived from nitric acid NO_5HO by the removal of water (then the water molecule was given the formula HO) and one oxygen (O) bond, i. e. by the removal of HO_2.

Zinin at first studied [22] α-nitronaphthalin, then called nitronaphthalaze by the Laurent nomenclature. By passing hydrogen sulfide into an alcohol solution of nitronaphthalaze, synthesized by Laurent, or first saturating the alcohol with ammonia to raise the solubility of the nitro compound and then treating the solution with hydrogen sulfide, Zinin obtained an oxygen-free nitrogen-containing substance of basic character, and gave it the name of naphthalidam (naphthalidine) and the formula $C_{20}H_{18}N_2$ (known now as α-naphthylamine). Zinin described in detail the properties of the new compound, its salts with mineral acids (salt with hydrochloric acid $C_{20}H_{18}N_2 + H_2Cl_2$ and with sulfuric acid $C_{20}H_{20}N_2 \cdot H_2SO_4$), and with oxalic acid $C_{20}H_{18}N_2 + 2C_2O_3 + 2H_2O$. From the chloroplatinate its molecular, or as they then spoke, atomic weight was calculated as being equal to 1798, which corresponds to the already indicated formula by the old equivalents. Later [23] Zinin studied the derivatives of naphthalidine. By treating an alcohol solution of nitrobenzene (nitrobenzide by the old terminology) with ammonium sulfide Zinin isolated a new base — benzidam $C_{12}H_{14}N_2$, for which the salts with sulfuric acid, with hydrochloric acid, with platinum chloride and with mercuric chloride were obtained. J. Fritzsche [24] recognized aniline in the substance obtained by Zinin, which he was able to synthesize from anthranilic acid (from indigo).

The German chemist A. W. von Hofmann quickly showed the identity of benzidam and aniline with the "crystalline" obtained in the dry-distillation of indigo (1826) and the "cyanol" isolated from coal tar (1834). With respect to this work [22] of Zinin's, von Hofmann had the following to say [7]: "Even then we all sensed that the discussion was about a reaction of unusual importance ".

In the first paper Zinin mentioned his experiments on the reduction of nitronaphthaleze (dinitronaphthalene), but their more detailed description was given in the second paper [25] on amines. Here, under the conditions indicated in the first paper (a saturated alcohol solution of ammonia and hydrogen sulfide), from nitronaphthaleze $C_{20}H_{12}N_4O_8$ (dinitronaphthalene) was obtained seminaphthalidam or seminaphthalidine (naphthylenediamine), for which analysis gave th formula $C_{10}H_{10}N_2$. The salts of this base were prepared and its behavior toward different reagents (nitric acid and others) was studied. In a later paper [26] the purification of napthylenediamine (seminaphthalidine) was described.

Zinin remarks that ". . . in the formation of the described base the atomic weight of this substance ($C_{20}H_{12}N_4O_2$ decreases in half, since $C_{10}H_{10}N_2$ is obtained instead of $C_{20}H_{20}N_4$". From this remark can be seen the vague understanding of "atomic weight" in those times.

By extending his reaction to dinitrobenzide (m-dinitrobenzene) Zinin obtained a base that was easily oxidized in the air and to which he gave the name of semibenzidam (now m-phenylenediamine).

The third paper [27] on the reduction of nitro compounds contains the synthesis of m-aminobenzoic acid, which Zinin called benzamino acid, from nitrobenzoic acid (m-nitrobenzoic acid), and a description of the properties of the new base. He noted the identity in the compositions and the difference in properties of this new acid and Fritzche's anthranilic acid (o-aminobenzoic acid). The data on this amino acid were completed later [28].

In the same third paper was described the remarkable discovery of azoxybenzene and benzidine in the treatment with ammonium sulfide of azobenzide or azotobenzide (azobenzene), obtained by Mitscherlich (1834) in the form of handsome red crystals by the distillation of a mixture of their synthesized nitrobenzene with an alcoholic potassium hydroxide solution. By purifying the reaction products through the sulfate, which was then decomposed with boiling ammonia solution, Zinin obtained a new organic base with the composition $C_{12}H_{12}N_2$, which he proposed to call benzidine. The substance forms stable salts with mineral and organic acids, in which connection the sulfate proved to be nearly insoluble even in boiling water; the phosphate also showed slight solubility.

With respect to Mitscherlich's reaction, leading to azobenzene from nitrobenzene, Zinin came to the conclusion that "azobenzide is not the direct reaction product of potassium hydroxide on an alcohol solution of nitrobenzene". By mixing nitrobenzene with alcohol and dry powdered potassium hydroxide he obtained a new substance $C_{12}H_{10}N_2O$ – the yellow crystals of azoxybenzide (azoxybenzene), melting (m.p. 36°) into a strongly light-refractive liquid. It is known that later "liquid crystals" were studied on the example of azoxy compounds. In this same work and later [29] Zinin studied the nitration products of azobenzene (with subsequent ammonium sulfide treatment) and azoxybenzene, namely their mono- and dinitro derivatives, and also the reduction of azobenzene [26] with sulfurous acid to benzidine sulfate. Azoxybenzene was also reduced by reducing agents to benzidine. von Hofmann showed that benzidine is a diamine [31]. Later the action of hydrochloric acid on azobenzide (azobenzene) was described, where benzidine was obtained [30].

The formation of benzidine from azobenzene proceeds in a complicated manner. Hydrazobenzene is formed from azoxybenzene. In acid solution hydrazobenzene is isomerized into benzidine, which occurred in Zinin's experiments and was revealed by von Hofmann in 1863 [32]. The transformation of hydrazobenzene and its derivatives in acid medium into benzidine and its homologs is known as the benzidine and semibenzidine (semidine) rearrangements. After the studies of Zinin and von Hofmann appeared the investigations of P. P. Alekseev [33] and other Russian and foreign chemists on the formation of azoxybenzene and azobenzene from nitrobenzene and on benzidine.

For over 100 years now the Zinin reaction – the reduction of nitro compounds – has been extensively studied, being the base of the aniline-dye, pharmaceutical, and other industries, and the source of countless syntheses in the aromatic series. Each of Zinin's amines is the progenitor of a vast "genealogical tree" of intermediates and dyes in the chemical industry [34]. Zinin's discoveries are the cornerstone of this rich section of organic chemistry. The syntheses of amines by the Zinin reaction have been considerably modified, both here and abroad, and much has been done to elucidate the mechanism of this reaction.

Copulated and Coupled Compounds. In addition to the nitro compounds, being the substitution products of one pair of hydrogen atoms in the hydrocarbon by the nitric acid copula, Zinin also studied the sulfonic acids, which were also classified as being "copulated acids", where the water radical of sulfuric acid is replaced by a hydrocarbon radical. Nitrobenzene and benzenesulfonic acid were obtained by Mitscherlich. Zinin described the sulfonic acids of chloronaphthalene [22, 25]. The reaction for the reduction of nitro compounds to amines was also extended to the nitroparaffins. To elucidate the structure of the latter nitro compounds, Zinin, according to Butlerov [1], nitrated starch and then proposed to subject it to the action of ammonium sulfide, but, apparently, this investigation was never completed, since at that time some more accurate information had already been obtained that nitrocellulose and nitroglycerin were esters of nitric acid. It is known that the denitration of nitrocellulose for the purpose of regenerating cellulose is realized with the alkali sulfides (in the manufacture of nitro silk, etc.).

The amides of the acids – oxnaphthalide and formonaphthalide – were synthesized, which acids were already obtained in Kazan [1] by the coupling of naphthalidine (naphthylamine) with oxalic and formic acids [35]. In those same years Ch. Gerhardt studied the transformation of aniline oxalate (1845). The reaction for the acylation of amines possesses greatsignificance in synthesis work.

Developing the idea of Laurent and Gerhardt, Zinin studied the metaleptic substitution of the hydrogen in urea by organic acid radicals. He described (1854) the benzoyl derivative [by the old representation $C_2N_2(H_3C_{14}H_5O_2)O_2$] its acetyl derivative [$C_2N_2(H_3C_4H_3O_2)O_2$] and other monoureides [13]: butyryl- and valerylurea. Laurent and Gerhardt

(1850) obtained their benzoylureide by the reaction of benzoic aldehyde with urea, proving to be benzylidenediureide (Schiff, 1869).

Zinin realized the substitution idea also in the synthesis of acetylbenzoin and benzoylbenzoin [36] (copulation of benzoin with acidic groups); the absence of copulative hydrogen in the diketone benzil was noted by him. The formation of benzoin esters demonstrated the presence of the alcohol group in its molecule.

Of interest was the work of Zinin [37] on the artificial preparation (synthesis) of volatile oil of mustard (allyl isothiocyanate esters) and other allyl alcohol derivatives (compounds of the "propenyl series"), and specifically – the acetic and benzoic acid esters of allyl alcohol [38]. He tried to show the analogy of the "propenyl" radical with the ethyl and other radicals. Even earlier (1852) the reaction products of aromatic amines (by analogy with the ammonia reaction) with mustard oil [39] $C_8H_8NS_2$, were described, namely, the substituted thiocarbamides. From aniline was obtained the substance $C_{20}H_{12}N_2S_2$, and from naphthalidine the substance $C_{28}H_{14}N_2S_2$, (formulas are doubled). As a result, to Zinin belong the methods for the synthesis of mustard oil, thiocarbamides, esters of allyl alcohol, acylated amines and acid monoureides.

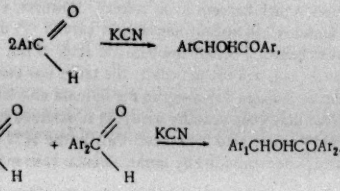
Synthesis and Reactions of Benzoin, Benzil and Desoxybenzoin. In his first papers [40, 41] (1839-1840) and in his doctoral dissertation (1841) Zinin [12] described the synthesis of benzoin from benzoic aldehyde under the influence of potassium cyanide and the conversion of benzil into benzilic acid under the influence of alcoholic potassium hydroxide solution. In subsequent years he repeatedly returned to the derivatives of benzoic aldehyde and benzoin. His last paper (1878), just like his very first studies, contains a description of some experiments with benzoin. The benzoin studies, the reduction of nitro compounds to amines and the other reactions discovered by Zinin are made one in the general problem of studying the reduction reactions of organic substances, the phenomena of the simultaneous oxidation-reduction of starting substances with the same or different molecular structures.

In his dissertation Zinin, on the basis of literature data and his own experiments on the benzoin condensation and the benzilic acid rearrangement, discusses the important and profound problem of the role of ferments* and catalysts. In his opinion [12], the transformations of substances under the influence of ferments and catalysts is due to the disturbance of the equilibria that are set up within certain limits in the vibrations of the atoms in molecules. Even earlier von Liebig [42] expressed the opinion that alcoholic fermentation is caused by the decomposition of the protein molecule of yeasts. In the words of Zinin, ". . . . . the decomposing substance is that body in which the decomposition process has already begun", and that ". . . in all of these processes the simpler cases of equilibrium take the place of the less stable". Using almond oil in his studies, he became interested in its formation from amygdalin and then turned his attention to mustard oil. Methods for the preparation of these oils [43] already existed at the time and data had been accumulated on the fermentative processes taking place here. Von Liebig and Wöhler [44] had obtained and elucidated the composition of benzoic aldehyde, which they had obtained from amygdalin in the presence of emulsin. Benzoic aldehyde (almond oil, known from 1803) had also been obtained earlier by the fermentative hydrolysis of the amygdalin from bitter-almond meal, the same as volatile mustard oil is formed from mustard meal (from the potassium salt of myronic acid) under the influence of a "proteinlike body" – the ferment "myrosin". As is known, amygdalin and potassium myronate belong to the glucosides, up to the 30's of the last century being obtained from the chemical treasures of the plant world. Zinin made a rich contribution to the study of benzoic aldehyde derivatives.

Benzoin From Benzoic Aldehyde. Even earlier a crystalline substance, called benzoin, had been obtained by treating raw almond oil with either lime or baryta water or with dilute potassium hydroxide solution. Zinin noted [41, 45] that benzoin is not formed from purified benzoic aldehyde ("benzoyl hydride") under the just indicated conditions, but if either potassium cyanide or sodium cyanide is added to an alcohol solution of pure aldehyde, then benzoin soon separates out as colorless crystals. This reaction, however, fails to proceed in the presence of silver cyanide, zinc cyanide and the metal chlorides. It was shown that the formation of benzoin in the old method of treating unrefined almond oil with the hydroxides of calcium, barium and potassium is due to the presence of hydrogen cyanide impurities in the unpurified oil, evolved, as is known, in the hydrolysis of amygdalin, together with benzoic aldehyde and sugar (gentiobiose). The hydrogen cyanide salts that are formed here function as the catalysts.

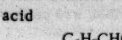
The Zinin reaction – the synthesis of benzoin from benzaldehyde in the presence of a specific catalyst, potassium cyanide – was later extended by various chemists to other aldehydes of the aromatic series;

*Enzymes.



This reaction was later called the benzoin condensation of aromatic aldehydes. Before the structure theory was applied to this group of compounds it was considered [17] that benzoin was a polymeric modification of benzoic aldehyde. In Zinin's studies on the preparation of the benzoin esters (see above) it was shown that the alcohol group is present in the molecule of this substance.

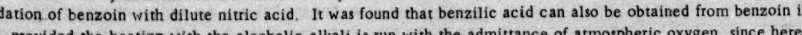
Zinin was greatly interested in the action of hydrogen cyanide on benzoic aldehyde, benzoin and benzil; some experiments in this direction had been made earlier by Laurent and others. Benzil, in Zinin's experiments [41, 45], forms benzyl hydrocyanide $C_{28}H_{10}O_4 \cdot 2HCN$ (here the actual number of atoms is doubled), while benzoin fails to react with HCN. The hydrogen cyanide derivative of benzaldehyde was obtained in admixture with benzoin when nearly anhydrous hydrocyanic acid was added to the aldehyde, with subsequent addition over several hours of an alcoholic "caustic potash" (potassium hydroxide) solution. According to Zinin, the composition of the substance can be seen from the following equation for the reaction: $3(C_{14}H_{12}O_2) + 2(C_2N_2H_2) - 2H_2O = C_{46}H_{36}N_4O_4$ or $C_{23}H_{18}N_2O_2$. A similar product was obtained by Laurent and named benzimide. Zinin later communicated [46] that benzimide is hydrolyzed into benzoic aldehyde and the amide of formobenzoyl $C_{16}H_{18}N_2O_4$ (or $C_8H_9NO_2$) acid (the amide of mandelic acid



By examining the action of hydrocyanic acid on benzoic aldehyde in the presence of fuming hydrochloric acid Zinin [47] isolated a substance with the composition $C_{15}H_{13}NO_2$, which decomposes on heating, forming the amide of formobenzoyl acid with the composition $C_8H_9NO_2$. These studies initiated the synthesis and study of the nitrile, amide, and even of mandelic acid itself, up to that time known as formobenzoyl acid.

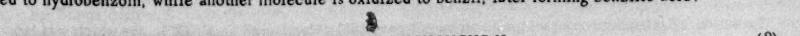
The addition reaction of hydrogen cyanide to benzoic aldehyde is of interest in connection with the problem of the mechanism of the benzoin condensation of aromatic aldehydes in the light of the hypothesis with respect to intermediate compounds and the activation of molecules under transformation [48].

Benzilic Acid. Zinin, at the request of von Liebig, looking for a convenient synthesis method of benzoin, studied the transformation, noted earlier by Laurent and studied more accurately by von Liebig, of benzil into benzilic acid in the presence of alcoholic alkali. The transformation can be depicted by the scheme:



(1)

Benzil was synthesized from benzoin, not by the Laurent method (action of chlorine on benzoin), but by the oxidation of benzoin with dilute nitric acid. It was found that benzilic acid can also be obtained from benzoin itself, provided the heating with the alcoholic alkali is run with the admittance of atmospheric oxygen, since here the benzoin is oxidized to benzil. Of interest is the fact that if benzoin is heated with alcoholic alkali in the absence of atmospheric oxygen [49], but at a somewhat elevated temperature (160-170°), that a small amount of benzilic acid and hydrobenzoin is formed. Consequently, under these conditions one molecule of benzoin is reduced to hydrobenzoin, while another molecule is oxidized to benzil, later forming benzilic acid:



(2)

Zinin defined the conditions of the benzilic acid rearrangement and also studied benzilic acid and its salts, showing, in particular, the red coloration that is obtained when benzilic acid is dissolved in concentrated sulfuric acid.

Zinin usually put in his first papers only the composition formulas of his studied compounds or more rarely the formulas that were based on the theory of radicals and the substitution theory, but these formulas were of little value for designating isomerism and isomeric transformations. Benzil was most frequently considered to be dibenzoyl

(polymer of the benzoyl radical), which happens to be correct. However, even at the end of the 1860's, when the chemical structure theory of Butlerov had already begun to be used in organic chemistry, some authors assigned completely incorrect formulas to benzoin, benzil and benzilic acid. Thus, the formula of dibenzoyl was assigned to a completely different substance [50], and not to benzil; the latter was assumed to be the anhydride of benzilic acid (of the α-lactone type), while to benzoin was assigned the formula now known for diphenylglycolic aldehyde [51], taking into consideration the fact that when benzilic acid [52] is oxidized it forms benzophenone, and when reduced with hydrogen iodide that diphenylacetic acid is formed. Only in the 1870's did it become clear that the transformation of benzil into benzilic acid is accompanied by intramolecular rearrangement.

In later years [53], based on the examples of diphenylglycolic aldehyde isomerization into benzoin and of diphenyl aldehyde into desoxybenzoin, new links were found in the chain of oxidative-reductive transformations from benzoin to benzil, and in reverse, also from benzil to benzilic acid, discovered by Laurent, von Liebig and Zinin.

The von Liebig-Zinin benzilic acid rearrangements can serve as a shining example of simultaneous intermolecular oxidation-reduction reactions, while the benzoin condensation belongs to the class of intramolecular (condensation) oxidation-reduction reactions [54].

Synthesis of Hydrobenzoin and Desoxybenzoin. In another group of papers, devoted to the derivatives of benzoin, are described the reduction of benzoic aldehyde, benzil and benzoin.

The hydrogen, evolved in the reaction of zinc with hydrochloric acid, and of iron with acetic acid, can reduce [55] benzil to benzoin (1861), and benzoin, and what is especially remarkable, benzoic aldehyde to hydrobenzoin, as had already been indicated at the start in the paper on the introduction of hydrogen into organic compounds [62] (1861) and later (1863) more completely [56]. Hydrobenzoin was given its name by Zinin for the reason that this substance is richer than benzoin by two hydrogen atoms. To obtain hydrobenzoin (the meso forms) it is convenient to use the reduction of benzoic aldehyde with zinc and hydrochloric acid, which method was perfected later [53].

The racemic stereoisomer of hydrobenzoin, known under the name of isohydrobenzoin, was synthesized later (Fittig); different authors gave different names to these glycols [57]. Zinin oxidized hydrobenzoin with nitric acid to benzoin. Thus, it can be seen that the Zinin method for obtaining α-glycols from aromatic aldehydes served as a pattern for the discovery of the synthesis of pinacones (pinacols) from ketones (pinacone from acetone), but of special interest is the reaction for the reduction, by the Zinin method [55], of benzoin to desoxybenzoin ("desoxidized benzoin") under the prolonged action of zinc and hydrochloric acid:

$$C_6H_5CHO \rightarrow C_6H_5CHOHCHOHC_6H_5 \rightarrow C_6H_5CHOHCOC_6H_5 \rightarrow C_6H_5CH_2COC_6H_5.$$

Desoxybenzoin is formed [58] under the prolonged action of hydrogen (zinc and hydrochloric acid) on benzoin. The distillation of benzoin gives desoxybenzoin together with benzoic aldehyde and benzil [59]; the latter can also be reduced to desoxybenzoin [56, 58].

Zinin also described the nitration product of benzil [60].

Derivatives of the Stilbene Series, and Halogen Derivatives of Benzil and Desoxybenzoin. In his general report [61] on the theory of the stilbene series (1868) Zinin examined the halogen derivatives of benzil and desoxybenzoin, and also the preparation of stilbene and tolane from them, remarking that different methods can be used to obtain substances of the stilbene (sym-diphenylethylene) series from benzoin. He showed that the action of phosphorus pentachloride on benzil results in the replacement of at first one, and then of the second, oxygen atom by two chlorine atoms. The action of phosphorus pentachloride on ketones (on the example of desoxybenzoin) is a typical reaction for the carbonyl group, but here the formation of unsaturated chlorides is also possible.

The action of phosphorus pentachloride on benzil gave [55] chlorobenzil $C_{14}H_{10}OCl_2$, for which was later given the structure $C_6H_5CCl_2COC_6H_5$. Further treatment with phosphorus pentachloride gave quadrichlorobenzil $C_6H_5CCl_2CCl_2C_6H_5$ or quadrichlorotolane [61]. The chlorine atoms in chlorobenzil are hydrolyzed when heated with water or with alcohol, in which connection benzil is formed. If the chlorobenzil in alcohol solution is treated with either zinc or tin (with the addition of hydrochloric acid, then desoxybenzoin ($C_{14}H_{12}O$), is obtained, being the best method for the preparation of desoxybenzoin from benzil [63]. Treatment of benzil with ammonium sulfide gives desoxybenzoin [64].

It is necessary to mention the valuable observation made by Zinin that metallic zinc reacts vigorously ("without the aid of either acid or alkali") with the chloro and bromo derivatives in different media, removing the halogen

atoms, in which connection unsaturated hydrocarbons are formed. In Frankland's experiments (1857) a similar reaction for the action of metals on chlorides led to the organozinc compounds, and not to the free radicals, and in Gomberg's investigations, made on the threshold of the 20th century, to the discovery of free radicals as exemplified by the action of metals on triphenylchloromethane. Here quadrichloronaphthalene (naphthalene tetrachloride) forms naphthalene, dibromostilbene forms stilbene, and dibromo- and dichlorotolane form tolane. By the action of zinc on quadrichlorobenzil we obtain the intermediate dichlorides ($C_{14}H_{10}Cl_2$), which are transformed by sodium amalgam into tolane [65]. If quadrichlorobenzil is treated in boiling alcohol with sodium amalgam, then the earlier known tolane is formed by the equation:

$$C_{14}H_{10}Cl_4 + 4Na \longrightarrow C_{14}H_{10} + 4NaCl.$$

An interesting new method for the preparation [61] of stilbene ($C_6H_5CH = CHC_6H_5$) is from the reaction product of phosphorus pentachloride with desoxybenzoin by its reaction with sodium amalgam; if the unsaturated chloride (α-chlorostilbene) obtained here is treated with potassium hydroxide under heating, then tolane is formed:

$$C_{14}H_{12}O \xrightarrow{PCl_5} C_{14}H_{11}Cl \begin{cases} \xrightarrow{Na} C_{14}H_{12} \\ \xrightarrow{KOH} C_{14}H_{10} \end{cases}$$

The direct chlorination and bromination of desoxybenzoin by the Zinin method [65] serve as a method for the synthesis of chloro and bromo ketones, containing the halogen in the α-position to the carbonyl: $C_6H_5CBr_2COC_6H_5$ and $C_6H_5CHBrCOC_6H_5$. It is known that later the mono- and dihalo ketones and the halo aldehydes began to be extensively used in syntheses.

It should be mentioned that the structure of desoxybenzoin as being phenyl benzyl ketone was conclusively established by Radziszewski [66]. An interesting characteristic of desoxybenzoin is the mobility of the hydrogen atoms adjacent to the carbonyl group, which was the reason for the formation of Zinin's benzamarone and amaric acid.

Alkylation and Condensation Products of Desoxybenzoin (Benzamarone and Amaric Acid). Zinin found (1870-1871) that desoxybenzoin is stable in aqueous alkali solutions [67] even at 180°, provided atmospheric oxygen is excluded, while in alcoholic alkali solution it suffers change more readily. In the case of prolonged exposure of desoxybenzoin in alkaline medium to atmospheric oxygen the formation of the potassium salts of benzoic and benzilic acid is observed and the separation of a new substance with the composition $C_{70}H_{56}O_4$, in the form of needles, which was named benzamarone. Under prolonged heating of benzamarone with alcoholic alkali at the boil the benzamarone suffered decomposition, forming desoxybenzoin in a new substance of acidic nature, soluble in alkalies, which Zinin named amaric acid. Its composition changes under heating due to the loss of water, in which connection the "anhydride" of amaric acid arises. In alkali solution the newly obtained substance was again transformed into the salt of amaric acid.

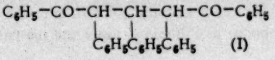
The numerous experiments on amaric acid and its analogs were described in a following paper (1877) [68]. Amaric acid, its salts and its "anhydride" were obtained in purer form. The alkali salt of amaric acid when heated to high temperature in excess alkali suffers cleavage into benzoic acid and a new product – pyroamaric acid. The "anhydride" of amaric acid when heated (to 200°) with alkali also formed pyroamaric acid, where gaseous hydrogen was also evolved. Amaric acid was assigned the formula $C_{46}H_{42}O_6$, its "anhydride" $C_{46}H_{38}O_4$, and the pyroamaric acid $C_{18}H_{16}O_2$.

Coming to the conclusion that the ethyl radical is contained in the amaric acid molecule, and taking into consideration the fact that the synthesis of benzamarone and amaric acid was run in ethyl alcohol, Zinin, to verify his postulation, made some experiments on the action of alkali on desoxybenzoin in various alcohols. It was found that the same benzamarone was always obtained. However, the heating of benzamarone itself with alkali in either ethyl or isobutyl alcohol gave different substances, depending on the nature of the alcohol. The previous amaric acid he began to call ethylamaric acid, while the acid obtained from benzamarone in isobutyl alcohol was named isobutylamaric acid (with compostion $C_{50}H_{46}O_4 + 2H_2O$). Isobutylamaric acid, similar to ethylamaric acid, when heated at elevated temperature with alkali suffered cleavage into benzoic acid and isobutylpyroamaric acid $C_{18}H_{20}O_2$.

Zinin assumed his pyroamaric acid to be "benzylethylbenzoic acid", isomeric with dibenzylacetic acid, and its isobutyl analog to be "benzylisobutylbenzoic acid". Zinin tentatively assigned structural formulas to his amaric anhydride and acid, which failed to receive confirmation later.

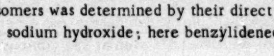
In his paper [67] Zinin mentions the work of the German chemists Limpricht and Schwanert [69], who, by treating desoxybenzoin with alcoholic potassium hydroxide, obtained the previously unknown acid $C_{18}H_{18}O_2$ and stilbene hydrate (phenylbenzylcarbinol) or stilbene itself, depending on the heating temperature. The investigation of the indicated authors was later continued by one of Zinin's students, A. Zagumennyi [70], who obtained in ethyl alcohol medium the diethylcarbobenzonic acid $C_{18}H_{18}O_2$ and studied it in greater detail than Limpricht and Schwanert. In propyl alcohol, desoxybenzoin under the influence of alkali gave the dipropylcarbobenzonic acid $C_{20}H_{22}O_2$ (the reaction failed to proceed in isopropyl alcohol), in isobutyl alcohol – the diisobutylcarbobenzonic acid $C_{22}H_{26}O_2$, and in amyl alcohol – the diamylcarbobenzonic acid $C_{24}H_{30}O_2$.

The structure of benzamarone and the amaric acids was elucidated considerably later as the result of the persevering efforts of a number of chemists. Benzamarone is obtained not only from desoxybenzoin (by the Zinin method), but also from a mixture of benzoin and desoxybenzoin [71] with alcoholic alkali, or from a mixture of benzil and desoxybenzoin [72]. It was found that an essential role in the formation of benzamarone is played by the benzoic aldehyde that is formed from desoxybenzoin, benzoin and benzil under the influence of alkali and atmospheric oxygen. The aldehyde condenses with desoxybenzoin through the two hydrogen atoms of the methylene group adjacent to the carbonyl group. It was established [72] that the formula given for benzamarone in Zinin's papers should be cut exactly in half ($C_{35}H_{28}O_2$ instead of $C_{70}H_{56}O_4$), and that benzamarone is the condensation product of benzoic aldehyde with two molecules of desoxybenzoin – it is benzylidene-bis-desoxybenzoin or bidesylbenzaldehyde (I), where, according to Knoevenagel [71], "desyl" refers to the desoxybenzoin radical.



(I)

Since two asymmetric carbon atoms are present in this formula, then stereoisomers are possible. Actually, in addition to the higher melting isomer obtained by Zinin (m.p. 225°), a lower melting isomer – isobenzamarone (m.p. 179-180°) – was isolated. Both isomers differ in their nitrogen-containing derivatives and in other properties. The structure of the stereoisomers was determined by their direct synthesis from benzoic aldehyde and desoxybenzoin in the presence of alcoholic sodium hydroxide; here benzylidenedesosoxybenzoin [73] (II) is also formed.



(II)

Benzamarone with isobenzamarone as impurity is formed in the reaction of benzylidenedesoxybenzoin with desoxybenzoin in the presence of alcoholate.

The studies of a number of scientists, made in the 80-90's of the previous century, elucidated the structure of amaric acid. Its molecular composition [74] is nearly one-half ($C_{23}H_{24}O_4$), that postulated by Zinin. The intermediate product in the transformation of benzamarone into amaric acid is benzylidenedesoxybenzoin, formed in the action of sodium ethylate on Zinin's amaric acid. When desoxybenzoin is treated with sodium methylate it fails to form the lower homologs of amaric acid. Klingemann [74] recommends the name of dimethylamaric acid for Zinin's isobutylamaric acid; the name amaric acid remains for the acid that was obtained by Zinin in ethyl alcohol. Amaric acid is oxidized to the dehydroamaric acids (α and β) of composition $C_{23}H_{18}O_2$, which forms pyroamaric acid when fused with an alkali, but without hydrogen evolution, in contrast to the transformation of amaric acid "anhydride". Klingemann was able to show that the amaric acids are not dibasic acids, but instead are monobasic hydroxy acids; their previously unknown derivatives were prepared.

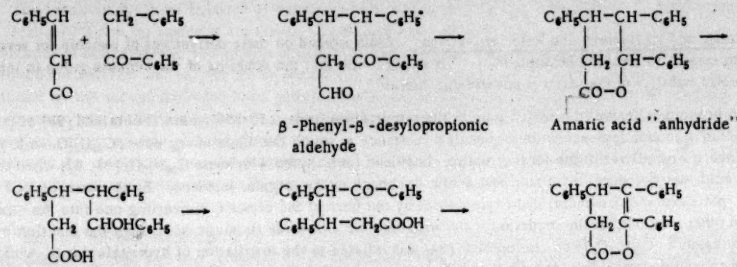
The problem as to the structure of the amaric acids, and also carbobenzonic acids, was solved [75] in Meerwein's studies. Both types of acids have a similar structure and similar formation path. The role played by the alcohols in the formation of the amaric and carbobenzonic acids consists in the initial formation of aldehydes, and then the products of their aldol condensation and crotonization. For the case of benzamarone transformation into amaric acids the benzoic aldehyde that is formed here, due to the cleavage of benzamarone and desoxybenzoin, can condense with aliphatic aldehydes. In the presence of alkali the desoxybenzoin then adds to the unsaturated aldehyde at the double bond, as a result of which the salt of the acid is formed, and from the acid is formed its lactone.

In his work Meerwein studied the condensation of unsaturated aldehydes and ketones with those aldehydes and ketones where the hydrogen atoms on the carbon adjacent to the carbonyl atoms are characterized by great mobility (ability to enolize [76]). He paid special attention to the structure elucidation of Zinin's amaric acid, diethylcarbo-

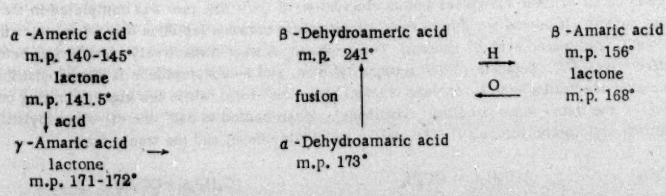
benzonic acid and related substances [75].

In the presence of sodium methylate both the unsaturated and saturated carbonyl-containing substances react in such manner that the 1,5-dialdehydes and 1,5-ketoaldehydes are formed, which, in the presence of the alcoholate, suffer smooth isomerization into lactones. Under the influence of alkali the latter form keto alcohols. Zinin's amaric "anhydride" is the 1,5-lactone (β, γ, δ-triphenylvalerolactone) of β, γ, δ-triphenyl-δ-hydroxyvaleric acid. Amaric acid is known in the form of 3 isomers; the isomer, obtained by Zinin, is known as α-amaric acid. It must be assumed that the "anhydride" of amaric acid is the lactone.

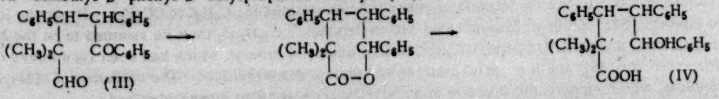
The mechanism for the formation of amaric acid consists in the oxidation of ethyl alcohol to the aldehyde, where the desoxybenzoin, cleaved from the benzamarone, is reduced to stilbene hydrate (phenylbenzylcarbinol) [77]. The oxidation of the alcohol in alkaline medium can also be accomplished with atmospheric oxygen. The benzoic aldehyde, formed under the conditions of the Zinin reaction, condenses with acetic aldehyde to form cinnamic aldehyde, to which the desoxybenzoin adds at the double bond with the formation of β-phenyl-β-desylpropionic aldehyde. Under heating in the presence of an alcoholic solution of a sodium alcoholate or at room temperature with alcoholic (methyl alcohol) alkali the latter product isomerizes (by an internal Cannizzaro reaction) into triphenylvalerolactone. An aqueous-alcohol alkali solution cleaves the lactone to the hydroxy acid. The hydroxy acid can also be formed from the aldehydoketone by the benzilic type of rearrangement. Dehydroamaric acid is obtained by the oxidation of amaric acid or by the oxidation of the ketoaldehyde [74]. All of these transformations can be shown by the scheme:



We will show a table of the indicated transformations (Meerwein):

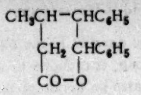


Also elucidated were the structure and possible path for the formation of dimethylamaric (Zinin's isobutylamaric acid) acid from benzamarone or desoxybenzoin when heated with an isobutyl alcohol solution of potassium hydroxide. Benzylidenedesoxybenzoin is formed either as the result of desoxybenzoin reacting with benzoic aldehyde or in the cleavage of benzamarone [74]. Isobutyric aldehyde adds to it at the double bond with the formation of α,α-dimethyl-β-phenyl-β-desylpropionic aldehyde (III).



Dimethylamaric acid ($C_{25}H_{26}O_3$) is α,α-dimethyl-β, γ, δ-triphenyl-δ-hydroxyvaleric acid (IV).

The carbobenzonic acids are formed in the same manner as the amaric acids, being obtained from desoxybenzoin by heating it with alkali in the media of various monoatomic alcohols. The theory was expressed that the intermediate stage in the synthesis of diethylcarbobenzonic acid is the formation of β-desylbutyric aldehyde via the coupling of the aldol with desoxybenzoin [78]. A more probable theory is that crotonic aldehyde plays an essential role here, to which molecule desoxybenzoin adds at the double bond; here β-desylbutyric aldehyde is formed, which then isomerizes into the lactone. Diethylcarbobenzonic acid (α and β) is β-methyl-γ, δ-diphenylvalerolactone (V):



(V)

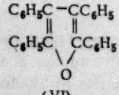
The other carbobenzonic acids are similarly constituted, and in their nature are close to the amaric acids.

The structure of Zinin's pyroamaric acid was also elucidated. It is also formed in the fusion of dehydroamaric acid with alkali [74]. It was found that pyroamaric acid is not ethyldiphenylacetic acid, but instead is some isomer of it. It was shown [79] that Zinin's pyroamaric acid should be recognized as being the lactone of β, γ-diphenyl--γ- hydroxybutyric acid, probably formed via ethylidenedesoxybenzoin from desoxybenzoin as a result of its condensation with acetic aldehyde. As was already shown, the amaric and benzoncarboxylic acids are formed by a similar scheme.

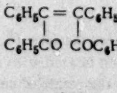
Lepidene and Its Hydroxy and Halo Derivatives. Zinin worked on these derivatives of benzoin for several years. With respect to lepidene he wrote [80]: "It seems to me that the doubling of the benzoin group in lepidene and the greater stability of the latter is not without interest".

When benzoin is heated in a sealed tube in the temperature limits 130-170° there is obtained [80] as the result of the oxidation and desoxygenation of benzil a substance to which the name of lepidene ($C_{28}H_{20}O$, m.p. 175°) is given, since it crystallizes in the form of scales. Lepidene forms hydroxylepidene $C_{28}H_{20}O_2$ [81, 82] when oxidized with nitric acid, easily reduced with zinc and acetic acid back to the original lepidene. Zinin characterized the needlelike, platelike and octahedral hydroxylepidenes by the form of the crystals, converting one into the other by heating and other methods. If the oxidation is run with chromic anhydride in acetic acid, then the reaction product is dihydroxylepidene $C_{28}H_{40}O_3$ [83]. Isolepidene [84] was isolated in the distillation of hydroxylepidene, which can be oxidized to hydroxyisolepidene and dihyroxyisolepidene and reduced to isolepidene dihydride and tetrahydride. Lepidene was obtained quite recently [85] by I. Ya. Postovsky and B. P. Lugovkin when they heated benzoin with aluminum powder.

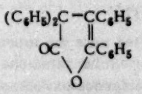
Further information on all of these substances and an elucidation of their structure was completed in the later studies made by various authors. It proved possible to show a relationship between lepidene and thionessal – the sulfur analog of lepidene [86], synthesized even by Laurent. These substances were respectively classified as being furan and thiophene derivatives [87]. Lepidene (VI) is tetraphenylfuran, and hydroxylepidene is dibenzoylstilbene (VII). Zinin's low-melting needlelike hydroxylepidene is taken as the cis- form, while the higher-melting octahedral hydroxylepidene belongs to the trans- forms (isodibenzoylstilbene). When heated to 340° the cis-dibenzoylstilbene is isomerized to the tetraphenylcrotonolactone (VIII) (platelike hydroxylepidene) and the trans- form.



(VI)



(VII)



(VIII)

Dihydroxylepidene was assigned the formula of phenyltribenzoylmethane: $C_6H_5C(COC_6H_5)_3$. It may no longer be reduced to lepidene [81]. Zinin's "hydrogenated hydroxylepidene" $C_{28}H_{22}O_2$ must be assumed to be the hydrogenated dibenzoylstilbene: $C_6H_5COCH(C_6H_5)CH(C_6H_5)COC_6H_5$, otherwise bidesyl, which had been synthesized earlier directly from desoxybenzoin [88], and from desyl bromide and sodium desoxybenzoin. The oxidation of bidesyl yields hydroxylepidene, which supports the structure of hydroxylepidene as being dibenzoylstilbene.

The proposed [89] complex formulas (bicyclic structures) with ether oxygen atoms in the furan nucleus, and

also the even older formulas with the cyclobutadiene nucleus for lepidene, hydroxylepidene and bihydroxylepidene proved to be worthless. For the purpose of elucidating the structure of the benzoin condensation products a study of their methylated derivatives was made; but here the treatment of the benzoin with hydrogen chloride in methyl alcohol solution gave the methylated tetrahydrofurans [90], and not the furan derivatives.

The chloro and bromo derivatives of lepidene and hydroxylepidene are described in Zinin's papers. Other authors later expanded the description of such chloro and bromo derivatives [89, 91]; however, even at the present time the structures of some of Zinin's compounds have not been fully established.

Significance of N. N. Zinin's Works in the Development of Condensation Reactions. Zinin's studies on the benzoin condensation of benzoic aldehyde and on the complex products, obtained from desoxybenzoin and benzoin, were the beginning of a wide study of the reactions based on the mobility of the hydrogen atoms in such carbonyl substances as desoxybenzoin, the nitriles and the hydroxy-carbonyl compounds. In studying Zinin's substances and the reactions discovered by him, different investigators found new examples of similar condensation reactions, which helped in delving into the nature of benzamarone, the amaric and carbobenzonic acids, lepidene, hydroxylepidene, etc. Zinin made these studies in that period for the inculcation of A. M. Butlerov's chemical structure theory into the study of organic compounds when there still failed to exist clear paths for establishing the structure of comparatively complex compounds, and for this reason he was unable to give the true structural formulas for the indicated group of substances. This makes complicated a study of the scientific inheritance left by Zinin in the different portions of his extensive investigations, needed in making a detailed historical survey of his activities.

The reactions for the alkylation of desoxybenzoin with alkyl halides in the presence of alcoholates, worked out by V. Meyer [92] and his students, are directly associated with the substitution condensation reactions having place in the synthesis of benzamarone and amaric acid. Under the influence of alkyl halides desoxybenzoin forms only monosubstituted derivatives, and only in phenyldesoxybenzoin, otherwise triphenylethanone, could another alkyl group be substituted for the second hydrogen atom found in the methylene group of desoxybenzoin [93]. In the synthesis of benzamarone both of the desoxybenzoin hydrogen atoms come singly from two separate desoxybenzoin molecules. In the synthesis of the amaric and benzoncarboxylic acids the condensations are also realized at the expense of one hydrogen atom in the methylene group of desoxybenzoin. However, in the case of benzylidene-monodesoxybenzoin both hydrogen atoms of the desoxybenzoin molecule are removed as water with the oxygen atom from the benzoic aldehyde.

Reactions for the condensation [94] of benzoin with nitriles, with ketones and with other substances as, for example, benzyl cyanide and acetophenone, were realized in the presence of either potassium cyanide or alcoholic alkali. In the case of acetophenone the diketone – (1,4)-desylacetophenone – is formed first, which in the presence of sulfuric acid is then converted to triphenylfuran. The reaction of benzoin with acetone [95] in the presence of alcoholic alkali proceeds in a similar manner, in which connection the first formed benzoic aldehyde reacts with acetone to give benzylideneacetone, which then condenses with benzoin with the removal of water at the expense of the benzoin hydroxyl group and the hydrogen atom from the methyl group of the unsaturated ketone. Condensation products of benzil with ketones are also known [96]. As a result, the reactions studied by Zinin, dealing with the condensations of benzoic, aldehyde, benzoin, benzil and desoxybenzoin, both between themselves and with other compound, uncovered fruitful paths in organic chemistry for the development of condensation reactions (condensations).

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The name of N. N. Zinin is written in gold letters in the history of organic chemistry, not only by his famous reaction for the synthesis of aromatic amines from nitro compounds, but also by his many other remarkable discoveries.

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THE MENDELEEV PERIODIC SYSTEM OF THE ELEMENTS AND THE ELECTRON SHELL STRUCTURE OF ATOMS

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From the time that the periodic law of chemical elements was discovered (1869) the periodic system was depicted by D. I. Mendeleev in all of the editions of "Fundamentals of Chemistry" in two table variations – the short and the long. The basic problem of the periodic system was the position of the rare-earth metals, for which Mendeleev allotted "preliminary" positions in the 8-10 series of the system. Mendeleev writes [1]: "Here I still have not made up my mind on anything, and here I see one of the more difficult problems with which the periodic law is confronted . . . ." In 1901 the Czech chemist B. Brauner [2] proposed putting all of these elements in the same series as cerium; Mendeleev failed to reject such a possibility but deemed it necessary to "leave this question open". Later, toward the end of the 20's, there appeared a number of tables of the periodic system, in which the rare-earths were taken out of the system and placed at the bottom as a separate line; similar to the lanthanoids, in our time the actinoids have also begun to be regarded as a separate series, and placed outside the system. As a result of this about 25% of all of the elements have been removed from the system, which stands in distinct contradiction to the spirit of the periodic law.

In recent years the following tendencies have been observed: 1) the putting back of the lanthanoids and actinoids into the system as being fully lawful members of it; 2) the use together with the short table of tables with irregularly developed periods, and 3) the showing of the interrelationship between the position of the element in the system and the electron structure of its atom.

Contemporary chemistry, in studying the properties of the elements, cannot be satisfied with only the positions of the elements in the system, but instead utilizes the electron structure of their atoms, made detailed by sublevels (for example, comparing the possible valence forms of fluorine and chlorine, of oxygen and sulfur, etc.). The position coordinates of the elements in the system should be synonymous and should answer to the real physical meaning, emphasizing the electron structure characteristics of their atoms.

The numbers 2,8,8,18,18,32 and (32) corresponding to the number of elements in the periods of the system, have long been known and hardly evoke any sort of argument. On the contrary, in recent years these numbers have found support in the formulas proposed by A. F. Kapustinsky [3] and by D. A. Bochvar [4]. Naturally, when 18- and 32-membered periods are distributed in an 8-compartment system there should be a rupture of the periods. The limits of these fractures are exceedingly diverse and depend on the subjective viewpoints of the individual scientists. We will compare a number of tables, constructed on the principle of the "short" system. According to V. N. Kondratyev [5] and B. M. Kedrov [6], the series iron, cobalt and nickel are arranged in Group VII in the right-hand portion of the table. In the tables of S. A. Shchukarev [7] and I. P. Selinov [8] these same elements, as extragroup elements, are placed in the left-hand portion of the table, which agrees with the characteristic value of the limiting valence shown by these 9 elements (for ruthenium and osmium-8; for iron, iridium and platinum-6; and for cobalt, nickel, palladium and rhodium-4) and which found both theoretical and experimental support in a number of papers by B. F. Ormont [9, 10]. The rare-earth elements, representing a series of 14 elements in Period VI, are also arranged differently in the above-indicated tables: the "fracture" limits of the series are found at gadolinium, erbium and holmium, and in another table composed by Selinov [11] – at dysprosium. For the actinoids, as analogs of the lanthanoids, such a breakdown in distribution is characteristic. The element triads in Group VIII and a portion of the lanthanoids and actinoids are arranged in some of the tables in distinct series, and in other tables in ill-defined series. If the number of the period shows the number of electron levels in the atom of the element, and if the number of the group shows the number of external or valence electrons, then in the structure aspects of the atom the series fails to show anything, and it can validly be excluded from some of the tables [5, 8].

The most well-based and distinct variation of the "short" system is the table of Shchukarev, in which the individual position of d- and f-elements is emphasized. The decads of the d-elements in the IV, V and VI periods are divided into 2 groups of 5 elements each, which is found to be in accord with the Hund rule and corresponds to

THE D.I. MENDELEEV PERIODIC SYSTEM OF THE ELEMENTS

Periods		Subgroups of the elements: I	II	IIIA	Series of intergroup elements
	Higher salt-forming oxides	R_2O	RO	R_2O_3	R_xO_y
	Higher gaseous hydrogen compounds				
I		H 1 1.0080	He 2 4.003		
II	s^2	Li 3 6.940	Be 4 9.013		
III	s^2	Na 11 22.997	Mg 12 24.32		
IV	s^1	K 19 39.100			
	s^2		Ca 20 40.08	Sc 21 44.96	
V	s^0				
	s^1	Rb 37 85.48			
	s^2		Sr 38 87.63	Y 39 88.92	
VI	s^1	Cs 55 132.91			
	s^2		Ba 56 137.36		Lanthanoids: Ce 58 140.13; Pr 59 140.92; Nd 60 144.27; Il 61 (145); Sm 62 150.43; Eu 63 152.0; Gd 64 156.9; Tb 65 159.2; Dy 66 162.46; Ho 67 164.94; Er 68 167.2; Tu 69 169.4; Yb 70 173.04; Lu 71 174.99
	s^2d^1			La 57 138.92	
VII	s^1	Fr 87 (223)			
	s^2		Ra 88 226.05		Actinoids: Th 90 232.12; Pa 91 231; U 92 238.07; Np 93 (237); Pu 94 (242); Am 95 (243); Cm 96 (242); (243); Cf 98 (246); An 99; Cn 100
	s^2d^1			Ac 89 (227)	
Filling of sublevels p, d and f after		s-elements		■	f-elements
Quantum number of the last electron		s^1	s^2	d^1	f^2 f^3 f^4 f^5 f^6 f^7 f^7d^1 f^9 f^{10} f^{11} f^{12} f^{13} f^{14} $f^{14}d^1$

Subgroups of the elements

IVA	VA	VIA	VIIA	Intergroup elements	IA	IIA	III	IV	V	VI	VII	0	Filled sub-levels in given period
RO_2	R_2O_5	RO_3	R_2O_7	R_xO_y	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	--	
								RH_4	RH_3	RH_2	RH	--	
											(H)	(He)	$1s^2$
							B 5 10.82	C 6 12.010	N 7 14.008	O 8 16.00	F 9 19.00	Ne 10 20.183	$2s^2p^6$
							Al 13 26.96	Si 14 28.06	P 15 30.975	S 16 32.066	Cl 17 35.457	A 18 39.944	$3s^2p^6$
		Cr 24 52.01				Cu 29 63.54							$3d^{10}$
Ti 22 47.90	V 23 50.95		Mn 25 54.93	Fe 26 55.85	Co 27 58.94	Ni 28 58.69		Zn 30 65.38	Ga 31 69.72	Ge 32 72.60	As 33 74.91	Se 34 78.96	Br 35 79.916	Kr 36 83.8	$4s^2p^6$
						Pd 46 106.7									$4d^{10}$
	Cb 41 92.91	Mo 42 95.95		Ru 44 101.7	Rh 45 102.91		Ag 47 107.880								$5s^2p^6$
Zr 40 91.22			Tc 43 (99)					Cd 48 112.41	In 49 114.76	Sn 50 118.70	Sb 51 121.76	Te 52 127.61	I 53 126.91	Xe 54 131.3	
						Pt 78 195.23	Au 79 197.2								$4f^{14}5d^{10}$
Hf 72 178.6	Ta 73 180.88	W 74 183.92	Re 75 186.31	Os 76 190.2	Ir 77 193.1			Hg 80 200.61	Tl 81 204.39	Pb 82 207.21	Bi 83 209.00	Po 84 (210)	At 85 (211)	Rn 86 (222)	$6s^2p^6$
															$5f^{14}6d^1$ $7s^2$

d-elements

d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}

p-elements

p^1	p^2	p^3	p^4	p^5	p^6

the fracture of a number of different properties, noticed in the studies of Biltz and Klemm [12]. By means of analogous considerations the lanthanoids and actinoids are divided into 2 subgroups, consisting of 7 elements each.

The tables of V. L. Albansky [13] and N. P. Agafoshin [14] hold a unique position. Albansky, in an 8-compartment table, arranged the lanthanoids and actinoids in a vertical position, rather than horizontally (the "superstructures" of Albansky coincide with the "installations" of Brauner), but here the change in the metal (basic) properties of the elements found in these "superstructures" fails to agree with the changes, characteristic for the two directions of the periodic system. In the variation proposed by Agafoshin only the elements of the 4 main subgroups (I, IV, VII and O groups) are arranged radially, corresponding to the mean values for the ionization potential of 4, 8, 12 and 16 eV. For the remaining subgroups the mean value of the ionization potential fails to agree with the position of these elements in the table.

In a survey paper, Kedrov [6], defending a clearly subjective viewpoint that only the "short" table of the periodic system has a right to exist, among other arguments presents the uniform change in the values of the maximum valence based on oxygen for the elements of periods II-V. According to Kedrov the ideal scheme is:

II period Li-F:	1 2 3 4 5 6 7,
III period Na-Cl:	1 2 3 4 5 6 7,
IV period K- Br:	1 2 3 4 5 6 7 8 1 2 3 4 5 6 7,
V period Rb-I:	1 2 3 4 5 6 7 8 1 2 3 4 5 6 7. (1)

In this scheme only one valence is given for each of the triads in group VIII which is contradictory to the actual case. Taking into consideration the actual maximum valence of the elements and regarding it from the modern point of view, instead of that expressed by Frankland, the actual scheme (the elements showing deviation from the ideal scheme are separate) appears as such:

II period Li-F:	1 2 3 4 **4 2** 1,
III period Na-Cl:	1 2 3 4 5 6 7,
IV period K-Br:	1 2 3 4 5 6 7 **6 4 4 3** 2 3 4 5 6 **5**,
V period Rb-I:	1 2 3 4 5 6 7 8 **4 4 3** 2 3 4 5 6 7, (2)

i. e. deviation is observed for 11 elements (24%). It should be mentioned that Kedrov avoided extending his scheme to the elements of periods VI and VII, in which the change of valence, to be sure, in no way corresponds to his ideal scheme and would have led the author into confusion.

In his published paper Mendeleev [15] remarks: ". . . in addition to the minor and major periods there are also tertiary periods . . .".

A table, containing about 30 elements in period VI, was first composed by Thomson in 1895. Unfortunately we do not find any evaluation of this variation of the periodic table in Mendeleev's studies. In the 20's of this century this variation was taken as the base for constructing the system on the basis of atomic structures: the different series in it were divided into "framework" and "rare-earth" elements. Proceeding from this variation of the system, the number of rare-earth elements was accurately determined and an indication was given of the possible natural sources for the 72nd element, as being an analog of zirconium. Actually, the element hafnium was found in zirconium mineral concentrates.

In the construction of this type of table it was postulated that the atom of the following element differs from the atom of the preceding element by one electron, occupying a position in the lowest quantum level or sublevel. Actually, the d sublevel shows first electron completion for the 21st element (Sc), and not for the 19th (K); the f sublevel is filled first for 58 (Ce), and not for 49 (In). Proceeding from a statistical model of the atom, Fermi [16] showed that the full number of electrons with azimuthal quantum number k in an atom with order number Z is determined by the formula: $N_k = 2\left(\frac{6Z}{\pi^2}\right)^{1/3} k\Phi(\alpha)$, where $\Phi(\alpha)$ is the Fermi function *. The curves, constructed from Fermi's data, permitted determining the atoms in which the new sublevels are filled with the first electron: 1 H(s), 5 B(p), 21 Sc(d) and 55 Cs(f) and proved to correspond to the mean value of the multiple broken lines, found from the experimental data of Stoner [28]. In the (attached) figure the ideal successive filling with electrons

* At the present time more accurate formulas have been proposed by D. D. Ivanenko and S. I. Larin [17] and by V. M. Klechkovsky [18].

of the atomic sublevels s, p, d and f in elements is depicted by dotted lines. The actual filling of the sublevels with electrons is shown in this figure by continuous lines; the areas of deviation are shown cross-hatched

Of the tables of the periodic system, corresponding to the ideal distribution of electrons in the sublevels, mention should be made of the tables prepared by Ya. I. Mikhailenko [19], A. F. Kapustinsky [20], and others. In principle the table of A. E. Shtandel [21] fails to differ from the preceding, but is given in more detail. It seems possible to construct such a variation of the table as would have all of the elements included in it, arranged by periods with the numbers 2, 8, 8, 18, 18, 32 and (32), from which a detailed electron structure of the atoms in elements could be easily determined and, most important, the position of the elements that would correspond to the actual filling with electrons of the atomic sublevels found in the given element. Such a variation of the table is given below. In this table all of the known elements are included in the order of increase in their order numbers from 1 to 100. In accord with our postulations [22], the symbol Md* is taken for the 97th element. All of the compartments in the table are occupied; it is possible to synthesize elements with Z greater than 100. Period I consists of 2 elements, in the atoms of which the sublevel 1s is filled. In the atoms of the elements in periods II and III, after 2s and 3s sublevels are filled, the 2p and 3p sublevels are filled with 6 electrons each. It should be mentioned that if in the other periods also the quantum levels of the atoms would be filled only with s- and p-electrons, we would have the ideal 8-compartment periodic system. However, in period IV the completion of the electron level becomes more complicated; the earlier unfilled 3d sublevel wedges itself between the 4s and 4p sublevels, in its energy characteristics being close to the other two. Among the d-elements of this period the chromium and copper are different, in the atoms of which there is only one 4s-electron, and the number of 3d-electrons is one greater than the normal number. In period V the order of filling the sublevels is similar, but somewhat complicated by the ratio between the number of s- and d-electrons. Only for the 4 elements – yttrium, zirconium, technetium and cadmium – is the number of s-electrons equal to 2 (in the outer level) and the number of d-electrons normal; for niobium, molybdenum, ruthenium, rhodium and silver the number of d-electrons is one greater than normal, and there is only 1s-electron for each in the outer level. The 5s-electrons are absent in the palladium atom, and the number of d--electrons is two greater than the normal number. Even greater complication is observed in period VI: in the atoms of the elements the electrons of the 4f and 5d sublevels wedge themselves in between the 6s and 6p sublevels, in their energy characteristics being close to that possessed by the electrons in the other two sublevels. In the atoms gadolinium and lutecium the f-sublevel is filled after s^2d^1; in the platinum and gold atoms the number of d-electrons is one greater than normal, and only a single s-electron is found in each external quantum level. Period VII repeats the structure of the atoms in period VI, only instead of the 4f and 5d sublevels the 5f and 6d sublevels are filled with electrons.

In the proposed table 4 groups of elements stand out clearly: the s-, p-, d-, and f-elements. The nonmetallic elements are concentrated among the p-elements with the exception of the inert gases. The metallic elements are mostly concentrated among the s-, d- and f- elements. From the studies and views of A. N. Nesmeyanov [23], and of K. V. Astakhov and A. M. Kabakchi [24], it is known that the alkyl organometallic compounds can form only the s- and p-elements, which is shown in well-blended form in the table (the 3 transition elements should also be classified with them, and specifically zinc, cadmium and mercury, all possessing a completed d-sublevel).

The p-elements are compactly grouped in the right-hand portion of the table, the property changes for which are specifically along the verticals, corresponding to the Byron secondary periodicity phenomenon, recently finding experimental confirmation in the thermochemical studies of Shchukarev and co-workers [25].

As is known, the elements of the "d-family" are characterized by a variable valence in the compounds, formed, as a rule, from colored ions, possessing high polarization properties and a sharply defined tendency for complex-formation, para- and ferromagnetic properties, etc. The iron, cobalt and nickel subgroups occupy a special position, called by us intergroup elements of the oxide type R_xO_y, since each of these elements manifests an individualized valency, for most of them not associated with the number 8 (we exclude group VIII from the abridged subgroup). The elements, in the atoms of which the d sublevel is half-filled (d^5), are divided by the family of d-elements into two subgroups (heavy line), since, in accord with the Hund rule, a maximum number of free electrons is found in the Mn, Tc and Re atoms. Independent of the period number (IV, V, VI) and the number of d-electrons in the quantum level adjacent to the outer layer, in the atoms of the elements only three subgroups – IVA, VIIA and IIA – correspond to the value of the quantum number of the last electron (see the bottom line in the table). The abnormally filled d sublevels are underlined with two dashes. The atoms in the elements of periods

* The American scientist G. Seaborg proposed the name of mendelevium for the 101st element.

IV, V and VI, arranged in the horizontal line with designation "s^{2}", have the normal number of d-electrons; those placed in the horizontal line with designation "s^{1}" contain a number of d-electrons greater by one than the indicated quantum number of the last electron and, finally, in the palladium atom (the horizontal line designated "s^{0}") the number of d-electrons exceeds the normal number by 2. It appears both fundamental and necessary to make a further study of the specificity of the properties of the 10 d-elements (chromium, copper, niobium, molybdenum, ruthenium, rhodium, palladium, silver, platinum and gold) in connection with the abnormal filling of their atomic d-sublevels.

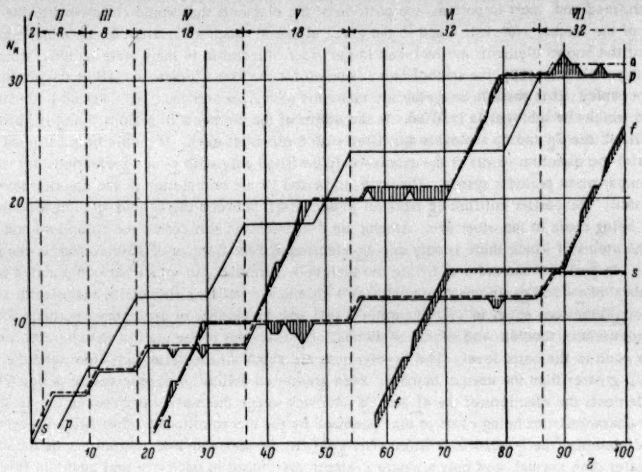

Figure. Filling of the sublevels in atoms with s, p, d, and f-elements.

In the table the lanthanoids and actinoids obtained their natural position as f-elements. These series we named "series of intergroup elements" with the R_xO_y type of oxide, since their positive valence changes from 2 to 4 (for the lanthanoids) and from 2 to 6 (for the actinoids). Gadolinium and curium divide these series in half, in accord with the Hund rule. In the lanthanoid series those elements should be similar that stand ahead of gadolinium and lutecium, and those that are arranged after lanthanum and gadolinium. The position of thorium still remains disputed: study of its spectrum fails to indicate the $f^{2}s^{2}$-electron configuration; it is possible that further studies will reveal its position more accurately.

The atomic electron structure for any element can easily be determined from the extreme righ-hand column given in the table ("Filled Sublevels in the Given Period") and the bottom line ("Quantum Number of the Last Electron").

The elements of the same subgroup appear as chemical analogs (vertical direction). The number of the subgroup determines the number of outer or valence electrons. He is an exception, which because of its s^{2}-eletron configuration was placed in group II (as is known, the spectrum of the helium atom is similar to the spectra of the alkaline-earth metals), but at the same time it is also noted, in parentheses, in the zero subgroup as an analog of the inert gases. Besides, the impossibility of being positively ionized in chemical reactions belongs not only to helium and the atoms of the inert gases, but also to the atoms of oxygen, fluorine and others. The arrangement of the elements by subgroups excludes the reasons for dissatisfaction with the 8-compartment system, which is expressed in such terms as " . . . in the incomprehensible falling of a number of elements into strange company, for example, manganese among the halogens. . ." [26], and also excludes the need for such remarks as: "In their chemical properties the metals of the copper subgroup have nothing in common with the alkali metals" [27]. The dual chemical nature of hydrogen permits showing it, in addition to its main position in subgroup I, as also having (in parentheses) a certain analogy with the halogens.

Double relationships between the elements can also be uncovered in the parallel examination of the subgroups: I–IA, II–IIA, III–IIIA, IV–IVA, V–VA, VI–VIA and VII–VIIA (i.e. the major and the minor subgroups).

SUMMARY

1. A table was proposed for Mendeleev's long-period periodic system of the elements, permitting all of the elements to be divided into 4 main types or families (s, p, d, and f).

2. In contradistinction to the known variations of the long-period system in the given table the elements are arranged in not only the order of increase in their order numbers, but also on the basis of their actual electron distribution among the atomic sublevels.

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TIN SULFIDES

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The two tin sulfides SnS_2 (mosaic gold) and SnS are well known in the literature, being found in nature as the mineral herzenbergite. The structural diagram of the system tin-sulfur [1] was studied only for the Sn-SnS portion, since in the region of higher sulfur contents the studies of this system encounter considerable difficulties. Postulations as to the existance of sulfides, lying intermediate between SnS and SnS_2, have been expressed, but have remained without confirmation.

In 1833 Berzelius [2], on heating stannous sulfide with sulfur, obtained a greenish mass, in which the atomic ratio of sulfur to tin was close to 1,5: 1. Later attempts [3] to repeat this experiment proved unsuccessful.

When the dissociation pressure of SnS_2 was studied by the method of static compensation [4] an isotherm (700°) was obtained, the character of which, in the opinion of the investigators, confirms the existence of Sn_2S_3 and Sn_4S_5, or of solid solutions that are comparable to them in composition. The authors [5], studying a mixture of tin sulfides by the microscopic method, communicate that they not only detected Sn_2S_3, but also synthesized it; however, neither the method of synthesis nor the composition of their preparation was published by these authors.

The intermediate sulfides of tin can be depicted as thiostannates, in which the cation is divalent tin, for example, $SnSnS_3$ or Sn_2SnS_4; their existence is probable from this viewpoint.

The absence of reliable data on the course of the thermal dissociation for SnS_2 makes it difficult to study the thermal constants of this sulfide, for which there are insufficient data in the literature.

The purpose of our work was to study the course of thermal dissociation for SnS_2 and the phase composition of the products obtained in this manner.

EXPERIMENTAL

In the experiments described below the tin sulfide was decomposed by heating in an atmosphere of dry purified argon, and its dissociation products obtained at different temperatures were studied by the microscopic and x-ray structure methods. In addition, the thermograms for the dissociation of SnS_2 in argon were registered.

The tin sulfide was prepared from electrolytic tin of 0-1 grade, pure flowers of sulfur and hydrogen sulfide, the latter purified by passage through chromic mixture. The tin was dissolved in hydrochloric acid (c.p.) and the stannous sulfide was precipitated from the obtained solution by the addition of hydrogen sulfide. The precipitate was washed with water containing hydrogen sulfide, then with alcohol, ether, and vacuum-dried (residual pressure of about 1 mm) at 200°. The dry stannous sulfide was mixed with flowers of sulfur in the ratio of 2: 1 and then heated in argon at 500-550° for 30 minutes. In this way we obtained several preparations of SnS_2 with a total sulfur and tin content of 99.70-99.95 %, and with an atomic ratio of S: Sn 1.98-2.02. The direct precipitation of SnS_2 with hydrogen sulfide, after the oxidation of $SnCl_2$ to $SnCl_4$ with chlorine, proved to be more complicated due to the poorer filtration properties possessed by the precipitate.

The thermograms for the dissociation of SnS_2 were registered with the aid of an N. S. Kurnakov pyrometer by the differential method. The samples, weighing about 5 g each, were protected from oxidation by the addition of dry purified argon, which beforehand had been passed through sulfuric acid, phosphoric anhydride and calcium turnings, heated to 600°. Reliably registered endothermal effects were obtained on the thermograms at 520, 635-645 and 740°; one of the thermograms is shown in Fig. 1.

The preparations for the microscopic and x-ray structure studies were prepared by the partial decomposition of SnS_2 in an argon atmosphere at various temperatures. The temperatures for this were selected from the thermo-

graphic data, i.e. those temperatures were chosen at which the formation of preparations with a variable phase composition could be expected. For this purpose the weighed tin sulfide sample was placed in a porcelain boat contained in a tube furnace and then heated in argon for a period of 1 hour, after which it was cooled, weighed, and again placed in the furnace, always attempting to achieve a weight loss that would correspond to the formation of a product with the desired composition. Before each weighing the boat was cooled in the cold part of the tube; its movement along the tube was realized with the aid of a porcelain rod, inserted through an airtight stuffing box. The preparation conditions for the products, their composition and their specific gravity, the latter determined with a pycnometer, are all given in Table 1.

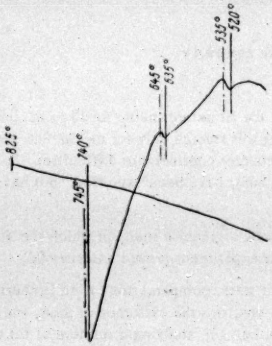

Fig. 1. Thermogram for the dissociation of SnS_2 (in argon).

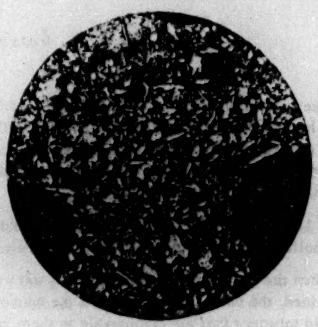

Fig. 2. Polished specimen of preparation No. 18 (500X). Light-gray color – very fine-grained mixture of SnS_2 tablet crystals, white color (predominant – Sn_2S_3), black color – cementing plastic mass.

TABLE 1

Preparations, Prepared for Microscopic and X-Ray Structure Studies

Preparation No.	Atomic Ratio S : Sn	Specific Gravity	Preparation Conditions	
			Duration of heating (in hours)	Temperature
1	2.01	4.61	–	–
23	1.97	4.45	2	500°
18	1.55	4.93	1	570
25	1.45	4.97	20.5	600
27	1.27	4.96	6	660
17	1.43	5.04	1	670
13	1.27	5.03	0.5	700
14	1.19	5.20	1	700
26	1.01	5.33	4	700
16	1.11	5.25	0.5	830
15	1.05	5.35	1	830
4	1.04	5.50	4	840

To be sure, the heating in a boat, even in an "immobile" gas, failed to exclude convection currents and therefore failed to assure equilibrium conditions for the sulfides in admixture with sulfur vapors, for which reason we did not figure on obtaining strictly individual substances; however, the postulated difference in the decomposition rates for the different sulfides permitted us to obtain products under these conditions that predominantly contained the desired compound.

The data given in Table 1 already elucidate the thermographic data to a certain degree. Actually, at 500° SnS_2 hardly changes in composition (initial $SnS_{2.01}$), while at 550° it already suffers appreciable decomposition in 1 hour. Consequently, its incipient decomposition at 520° is possible. Heating at 600° for 20.5 hours gives a product with a composition close to that of Sn_2S_3 while heating at 660° for 6 hours already makes the material much poorer in its sulfur content; this is verified by the fact that Sn_2S_3 shows incipient dissociation at 640°. Preparations Nos. 4 and 26 have practically the same composition, although the first was obtained at 840°, while the second was obtained at 700°. The thermograms fail to register any transformations in the interval 640-700°, consequently, there are no intermediate sulfides between Sn_2S_3 and SnS.

The microscopic studies of the dissociation products were made on polished specimens, under the microscope, using reflected light [6]. The powdery preparations were first briquetted with the plastic mass at 100° and moderate pressure, under such conditions as excluded a change in their composition and in the internal structural characteristics of the particles.

By microscopic study it was established that only three different components (Table 2) were present in the products obtained by us, which components are quite easily distinguished in the polished specimens by their properties. One of them is tin disulfide SnS_2 (mosaic gold), serving as the starting material in running the experiments. This sulfide is easily recognized under the microscope by its characteristic bright golden-yellow internal reflexes*. A second easily determined component is tin monosulfide SnS, which is obtained as the final, almost completely pure, dissociation product. This component is characterized by the lowest atomic ratio of S:Sn (1.04 for preparation No. 4 and 1.01 for preparation No. 26, Table 1). In its optical properties this component, whose analog in nature is the mineral herzenbergite, differs strongly from SnS_2; it possesses a sharply elevated refractive power and is practically devoid of internal reflexes.

The third component is manifested only in mixed two-component formations together with SnS_2 and SnS. From its role of intermediate component, and also by the intermediate character of its optical properties, when compared with the first two compounds, the third component is tentatively considered as being the tin sulfide of composition Sn_2S_3.

The postulation of the composition of the third component is governed by calculating the relative amounts of components in the two-component mixtures, using the method of solving the following system of equations:

$$A_1X_1 + A_2X_2 = A_{1-2} \cdot 100, \quad (1)$$

$$X_1 + X_2 = 100, \quad (2)$$

where: A — for the first and second are known, and for the third component are postulated, values of the atomic ratio S:Sn for two of the components (1 and 2) and their mixtures (1-2); and $\underline{X}$ are the relative amounts (in weight %) of two of the components in the mixture.

The relative amounts of the components present in the mixtures, calculated by this method, closely agree with the approximate visual determination made of these values (Table 2). The close agreement of the calculation results and the visual evaluations (and for some of the preparations the more exact planimetric measurements) was so constant as to offer conclusive evidence for the validity of the original postulation made as to the chemical formula of the third tin sulfide in the composition make-up of the products obtained by us.

In its physical diagnostic properties, Sn_2S_3 is quite distinctly different from the other two tin sulfides. In accord with the data given here (Table 3), the sulfide of composition Sn_2S_3 possesses optical properties that lie intermediate between those of the other two sulfides: in its reflective power (about 30%) it is noticably lighter than SnS_2, but darker than SnS; in contrast to both of the others, it possesses distinct dense reddish-brown internal reflexes.

The data available on the specific gravities of the end (one-component) and intermediate products in this series of experiments, and also the values obtained above for the relative amounts of components in the mixtures, make it possible to calculate the specific gravity of the sulfide Sn_2S_3. Such a calculation leads to an average value of 4.7 for this property. However, for the products with a sharp quantitative preponderance of Sn_2S_3 (preparations Nos. 18 and 25) the values obtained for the specific gravity lie close to 4.9.

* The internal reflexes of reflected light under the microscope characterize the capacity of substances for translucence and their color when illuminated.

TABLE 2

Substance Composition of the Dissociation Products

Preparation No.	Characteristic		Preponderant Components in the Mechanical Mixture *			Remarks
	Atomic ratio	Specific gravity	SnS_2	Sn_2S_3	SnS	
1	2.01	4.51	Practically homogeneous (100%)	–	–	Insig. amts.** of metallic tin, SnS and Sn_2S_3 Structure *** very fine-grained powder (~1 μ)
18	1.55	4.93	In subordinate amount (10%)	Sharply predominates quantitatively (90%)	–	Structure–uniform fine-grained (up to 10μ) powder (Figure 4)
25	1.45	4.97	–	Sharply predominates quantitatively (90%)	In subordinate amount (10%)	Structure–clumps of well-formed crystals (0.1-0.15 mm)
27	1.27	4.96	Insignificant impurity	Mixture of the two components in approximately equal amounts		Structure–same as No. 25 (Fig. 5)
13	1.27	5.03		(54%)	(46%)	Structure–fine crystals (0.05 mm) of SnS in finely divided Sn_2S_3 powder
14	1.19	5.20	–	In somewhat subordinate amount (38%)	Slightly predominates quantitatively (62%)	Structure–intermediate character between Nos. 27 and 13
4	1.04	5.50	–	–	Homogeneous (100%)	Structure–broken pieces (up to 0.5 mm) of coarse crystals
26	1.01	5.58	–	–	Practically homogeneous (100%)	Structure–parallel clumps of prismatic crystals (Fig. 5) Insig. amts. of FeS of the type of native pyrrhotine
5	–	–	Heterogeneous mixture of both components in substantial amounts	–	–	Structure–dimensions of the particles in the dispersed mixture are less than 1 μ

* The relative amounts of the components are indicated: in the text–by visual observation, in percents–by the calculation results from equations (1) and (2).

** Insig. amts. – insignificant impurities of other components.

*** Structure – structure of the aggregate.

TABLE 3

Characterization of the Diagnostic Properties of Artificial Tin Sulfides

Designation of the Properties	SnS_2 – "Mosaic Gold", No Natural-Occuring Analog; Hexagonal Syngony *, Form of Crystals – Scales, Leaflets	Sn_2S_3 – No Natural-Occurring Analog; Rhombic Syngony*, Form of Crystals – Tablets and Needles	SnS – Natural-Occurring Analog is the Mineral Herzenbergite; Rhombic Syngony*, Form of Crystals – Prismatic to Needle-like
Specific gravity (approximate, based on calculation results)	4.5	4.9	5.5
Reflective power (R %) and color in reflected light	R about 25%, the darkest gray of the three	R is about 30%, light-gray	R is about 40%, galeno-white
Behavior toward polarized light: a) with crossed Nicol prisms, b) double reflectance	Only in completely crystalline formations: a) very strongly anisotropic; b) shows very strong double reflectance, approximately in the limits of 35-18%	a) Distinctly anisotropic, but weaker than SnS, b) was observed distinctly only under immersion	a) Strongly anisotropic with a color effect, b) observed distinctly only under immersion
Character of internal reflexes	Always noticeable with the dry specimen; golden-yellow in the finely powdered masses, up to tarry-yellow in the coarser crystals	Colored brown in finely powdered masses, visible in the dry specimen; reddish-brown in the coarser crystals, visible under immersion	Practically none, only under immersion is a very dense (doubtful) brown color observed in the powder
Behavior toward polishing	Observed only in the finely powdered masses, lending themselves to polishing with difficulty	Polishes well, but in sheet-like aggregates poorer than SnS	Always polishes very well
Hardness	All three components are easily scratched by a sharp steel needle.		
Similarity with native minerals and differentiating characteristics	Very similar to auripigment, but differs in showing much stronger double reflectance	Differs sharply from comparable native minerals by a brown tone of the internal reflexes	Similar to the minerals of the boulangerite group, but differs in the absence of internal reflexes

* According to the data of [5].

Fig. 3. Polished specimen of preparation No. 27 (500X). Growths of spongy and platelike Sn_2S_3 aggregates (gray color) with prismatic SnS crystals (white color).

Fig. 4. Polished specimen of preparation No. 26 (500X). Parallel growths of prismatic SnS crystals (white color) in their cementing plastic mass (black color).

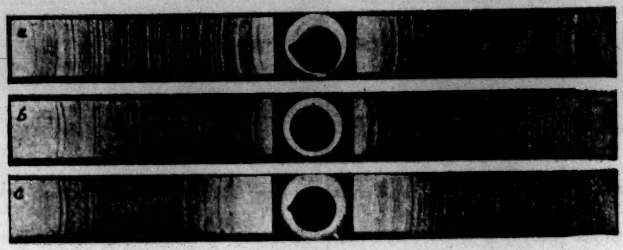

Fig. 5. X-ray patterns of SnS_2 and its dissociation products. a) - preparation No. 1 (SnS_2), b) - preparation No. 4 (SnS), c) - preparation No. 25 (mixture, composed of 90 % Sn_2S_3 and 10% SnS).

The full characterization of the diagnostic properties of the three tin sulfides studied by us (Table 3) testifies to the quite clearly expressed individuality of each one of them. In addition, a distinctly expressed rule for the change in the main optical constants (the reflective power and the absorption capacity) in this series of sulfides is established as a function of the atomic ratio S : Sn in their composition.

In conclusion, in characterizing the diagnostic properties of the artificial tin sulfides, it will also be necessary to mention the following: the diagnostic properties of the tin sulfides are characterized very superficially in the literature [5], without any indications relative to the essential differentiating characteristics of each. In the extensive description of mineral ores by Ramdor [7] a fairly detailed characterization of the properties of native tin monosulfide, the mineral herzenbergite, is presented, with reference being made to its close similarity with the artificial component of the identical composition. However, these data differ substantially from those obtained by us, in part corresponding to the properties observed by us for SnS, and in part to those observed for Sn_2S_3.

The x-ray structure phase analysis was executed by the powder method, in a standard chamber, using copper radiation. The characteristics of the studied preparations are given in Tables 1 and 2, and a facsimile of some of the x-ray patterns in Fig. 5.

A comparison of the x-ray patterns for preparations Nos. 4 and 26 confirmed the identity of these substances, and the error, permitted in measuring the distances between the lines, was also established. A total of 21 lines was registered for each of the two x-ray patterns, of which 4 lines were strong, 5 were average, and 12 were weak in intensity. The reflectance angles coincided with the maximum difference of 24', with the average value of the latter being 7.5'.

The x-ray pattern for SnS_2 (preparation No. 1) gives several reflectance angles, coinciding with the similar angles for SnS; however, the difference in the x-ray structure data for these two substances is quite distinct. To elucidate the structure of Sn_2S_3 we excluded from the x-ray pattern for preparation No. 25 the reflectance angles, peculiar to SnS, and obtained 17 lines in the remainder, of which 2 were strong, 1 was average, and 14 were of weak intensity. We were unable to calculate the parameters for the Sn_2S_3 lattice, since this sulfide crystallizes in the rhombic system, for which, as is known, the powder method fails to have any means of indicating x-ray patterns. The reflectance angles found for Sn_2S_3 in this manner were excluded from the x-ray pattern for preparation No. 27 and as a result 17 reflectance angles were obtained in the remainder, coinciding with the similar angles for SnS (preparations Nos. 4 and 26) within the limits of maximum error for the measurements.

As a result, the x-ray structure phase analysis confirmed the peculiar nature of the Sn_2S_3 structure and the presence of this sulfide in preparations Nos. 25 and 27. The x-ray patterns also showed a coinciding of the reflectance angles for pure SnS and preparation No. 26, which, as a result shows that the latter fails to contain any other tin sulfide or a solid solution.

SUMMARY

1. A phase analysis of the dissociation products of SnS_2 was made by the thermographic, microscopic, and x-ray structure methods.

2. Sn_2S_3 and SnS are successively formed in the thermal dissociation of SnS_2, and the presence of other sulfides or of solid solutions in the system tin-sulfur was not revealed.

3. The reciprocal equilibrium temperatures for the tin sulfides were determined: $2SnS_2 \overset{531^\circ}{\rightleftharpoons} Sn_2S_3 + \frac{1}{2} S_2$; $Sn_2S_3 \overset{610^\circ}{\rightleftharpoons} 2SnS = \frac{1}{2} S_2$.

4. Diagnostic criteria for the determination of artificial tin sulfides in polished specimens were established.

5. The specific gravity of Sn_2S_3 was determined by the calculation method, lying within the limits of 4.7-4.9.

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THE PREPARATION OF PHOSPHOTUNGSTIC ACID WITHOUT THE USE OF ETHER

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In recent years it has been possible to obtain the more important saturated heteropoly acids by direct synthesis, without resorting to the operation of extracting them with ether [1]. However, the preparation of phosphotungstic acid by the reaction of tungstic and phosphoric acids requires fairly prolonged washing of the H_2WO_4. In an attempt to simplify the etherless method of preparing phosphotungstic acid we verified and refined the method described in the literature [2], where two fairly close variations of the method for the synthesis of heteropoly acids through the barium salt are proposed. The treatment of a sodium tungstate solution with barium chloride gave barium tungstate as a precipitate (in 95% yield); the barium tungstate, suspended in water, was treated with a mixture of hydrochloric and phosphoric acids to give the trisubstituted barium phosphotungstate, which was then separated from the solution, washed, dried, and then again dissolved in water and decomposed with sulfuric acid. The obtained solution of phosphotungstic acid was evaporated under reduced pressure to yield the crystalline compound. In the second variation of the method the barium phosphotungstate is not isolated in the crystalline form, but instead is directly decomposed with sulfuric acid in the dissolved state; the yield of the heteropoly acid, according to the method of Philips [2], is theoretical.

EXPERIMENTAL

We checked both variations of the method; the basic equations for the process reduce to the following:

$$BaCl_2 + Na_2WO_4 = BaWO_4 + 2NaCl, \quad (1)$$

$$24BaWO_4 + 2H_3PO_4 + 21H_2SO_4 = 21BaSO_4 + 20H_2O + Ba_3H_8[P(W_2O_7)_6]_2, \quad (2)$$

$$Ba_3H_8[P(W_2O_7)_6]_2 + 3H_2SO_4 = 2H_7[P(W_2O_7)_6] + 3BaSO_4 \quad (3)$$

The first variation of the method for the preparation of barium tungstate was checked in the following manner: 1 kg of sodium tungstate, pure for analysis, was dissolved in 3.03 liters of boiling water, and to this solution was added a solution of barium chloride (758 g $BaCl_2 \cdot 2H_2O$ in 2.425 liters of boiling water). The solution containing the precipitated barium tungstate was cooled, the precipitate separated on a porcelain filter, then washed with hot water, and finally dried at 90-94°. The 1.3 kg of barium tungstate obtained in this manner was suspended in 2.031 liters of boiling water; 28 ml of phosphoric acid (87.9 %) was added to the suspension; the obtained mixture was boiled for 10-15 minutes, after which 812.5 ml of concentrated hydrochloric acid was added, and the mixture was stirred with a mechanical stirrer for about 2 hours. The preparation of the trisubstituted barium phosphotungstate was controlled by microscopic inspection and the reaction was considered as being ended when all of the barium tungstate had been converted into the octahedral crystals of the trisubstituted barium phosphotungstate. The $Ba_3H_8[P(W_2O_7)_6]_2 \cdot xH_2O$ precipitate was filtered on a porcelain funnel and washed with ice water; 1 kg of the air-dried barium phosphotungstate was introduced into 5 liters of boiling water and to this was added 27 ml of concentrated sulfuric acid and 250 ml of water; under constant mechanical stirring the solution was boiled gently for about 1 hour. The $BaSO_4$ precipitate was removed by filtration and washed with hot water; the complete removal of the phosphotungstic acid anion from the barium sulfate precipitate was checked by the method of adding 1-2 ml of quinoline acetate solution (100 ml of water, 2 ml of quinoline and 5 ml of concentrated acetic acid) to a test sample of the wash water; the filtrate, containing the phosphotungstic acid, and the wash waters were combined and evaporated to dryness under reduced pressure. The yield of the heteropoly acid was about 76% of the calculated amount.

The obtained acid was studied microscopically; its solution of 1: 20 was clear, and both the Ba^{++} and SO_4^{--} ions were absent (Preparation No. 1, Exp. 4).

We next turned our attention to the second variation of the synthesis method, since the advantage of this variation consists in the omission of the operations for isolating the trisubstituted barium phosphotungstate in crystalline form and in the use of hydrochloric acid for decomposing the barium salt; the addition of hydrochloric acid causes partial decomposition of the phosphotungstic acid anion and results in a reduced yield of the acid.

In checking the second variation of the synthesis method the barium tungstate was prepared in the same manner as described above; the analysis data for the amount of water in the air-dried salt are given in the Table (Preparations Nos. 1-3).

One kilogram of barium tungstate (calculated as being anhydrous was introduced into 912 ml of boiling water; 22.3 ml of phosphoric acid solution (d 1.722) was added under constant mechanical stirring, and the reaction mass was cautiously boiled for 15 minutes, the volume being kept constant by the addition of water. During the boiling the composition of the suspended solid phase was controlled by microscopic observation; here the process for the conversion of the barium tungstate into the crystalline trisubstituted barium phosphotungstate could be easily observed. After boiling for 15 minutes a solution of 145.6 ml of concentrated sulfuric acid (d 1.839) in 439 ml of water was added to the reaction mixture. Cautious boiling with stirrer mixing was continued for 2 hours. Then the hot solution was suction-filtered through a porcelain Buchner funnel; if the filtrate was obtained cloudy it was filtered again, having first added about 3 g of purified and pulverized carbon; the filtrate was evaporated under reduced pressure to dryness; the yield of the heteropoly acid was 80% of the calculated.

Analysis of this acid revealed that it had too high a P_2O_5 content (Experiment 5). After recrystallization the P_2O_5 content dropped down to that required by theory (Experiment 6).

The high P_2O_5 content was explained by the fact that in this experiment the amount of phosphoric acid and other reagents was taken in accord with the directions of Philips [2] and represented a 62.2% excess over the calculated amount; apparently, this excess of H_3PO_4 passed into the filtrate and contaminated the heteropoly acid obtained here; from our verification results it is easy to conclude that Philips never obtained the pure compound $H_7[P(W_2O_7)_6] \cdot xH_2O$.

Consequently, for the second variation of synthesizing phosphotungstic acid we took 16.3 ml of phosphoric acid (d 1.722) for 1 kg of anhydrous barium tungstate, which represented a 16% excess. The other operations were run in the same manner as had just been described for the first variation, except that the crystallization was run in a porcelain dish on the water bath at atmospheric pressure. The yield of the first crop of crystals was 76%; a second crop of crystals was isolated from the filtrates, the volume of which was about 250 ml, in a yield of about 13% (Experiment 7). In Experiment 8 the starting charge of barium tungstate was also 1 kg, but the amount of phosphoric acid taken was only 5% in excess of the theoretical. To obtain crystals the acid was evaporated to dryness on the water bath; the yield of the compound reached 83% of the calculated.

The analysis results for the obtained specimens show that compounds of definite composition are formed when a slight excess (5-10% of the calculated) of H_3PO_4 is used; however, the yield never reaches the theoretical figure, as is asserted by Philips.

TABLE

Analysis Results For the Obtained Barium Tungstate and Phosphotungstic Acid Specimens

Exp. No.	Designation Nos. for the barium tungstate preparations	Amount of H_2O (in %)	Amount of H_2O (in moles)	Amount of P_2O_5 (in %) Found	Amount of P_2O_5 (in %) Calculated	Yield (in %)
			Barium Tungstate			
1	1	1.23	–	–	–	98.0
2	2	1.09	–	–	–	97.5
3	3	1.14	–	for anhydrous composition	–	98.3
			Phosphotungstic Acid			
4	1	–	–	–	–	76
5	2	–	–	3.94	2.50	80
6	2*	8.81	14.65	2.58	–	–
7	3	14.11	23.50	2.61	–	89
8	4	11.65	19.40	2.63	–	83

* After recrystallization.

In the phosphotungstic acid preparations the amount of alkaline salts present, calculated as Na_2O, was less than 0.1%.

The amount of water present in the obtained phosphotungstic acid preparations varies from 14.65 to 23.54 moles; a variable water content is a common phenomenon for the preparations of various heteropoly compounds. It was established in earlier studies [3] that the water, bound in the molecules of heteropoly compounds as either solid solutions or as hydrates, is metastable, and for this reason the preparations of heteropoly compounds usually contain variable amounts of water.

SUMMARY

1. A method was developed for obtaining phosphotungstic acid through the barium salt without having to use ether.

2. The yields of the heteropoly acid reach 76-89%; in their composition the preparations correspond to the fully saturated acid.

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COMPLEXES OF PHOSPHORUS PENTACHLORIDE WITH SOME METAL CHLORIDES

II. SYSTEM PHOSPHORUS PENTACHLORIDE-ALUMINUM CHLORIDE (FERRIC CHLORIDE)-NITROBENZENE

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Phosphorus pentachloride possesses great interest as a study object in the chemistry of complex compounds. This is conditioned first of all by its structure characteristics and by the peculiar nature of its chemical properties. The individual phosphorus pentachloride molecules have a trigonal bipyramidal structure [1] in both the liquid and gaseous states. In the crystalline state PCl_5 consists of tetrahedral cations $[PCl_4]^+$ and octahedral anions $[PCl_6]^-$ [2].

In its reactions with other substances phosphorus pentachloride can react both in the form of $PCl_3 \cdot Cl_2$ – as an oxidizing agent, and in the form of $[PCl_4]Cl$,* in which connection it is indicated [1] that the first type of reaction proceeds at elevated temperature, while the second type of reaction proceeds at room temperature.

Such a mobility for the structure of PCl_5 creates the possibility of realizing various chemical reactions with its participation, in which number the complex-formation reaction is included.

There is basis to expect that in the reaction of phosphorus pentachloride with the chlorides of other elements, or with the chlorides of nitrogen bases, that two types of complex chlorides can be obtained: those containing the phosphorus in the form of the cation $[PCl_4]^+$ or in the form of the anion $[PCl_6]^-$. Among the double halides only a comparatively small number of cases are known up to now, being those cases where the halide of the same element manifests a similar dual function. However, as yet phosphorus pentachloride has been studied very slightly as a complex-former in the reactions with the halides of other elements.

A number of phosphorus pentachloride complexes with the chlorides of certain elements have been described in the literature. The following chlorides form equimolar compounds with phosphorus pentachloride: $AuCl_3$ [4], BCl_3 [5], $AlCl_3$ [6,7,8], $SnCl_4$ [7,9], $TiCl_4$ [6,10], $SbCl_5$ [7,11,12], $AsCl_3$ [11], $BiCl_3$ [7], $SeCl_4$ [7], $TeCl_4$ [13], $CrCl_3$ [11], $MoCl_4$ [11], $MoCl_5$ [14], WCl_4 [11], UCl_5 [11], ICl [7,15,10], IBr [17], $FeCl_3$ [6,7,11], and $PtCl_4$ [7]. The chlorides of mercury, zirconium and molybdenum form compounds having the composition $3HgCl_2 \cdot 2PCl_5$ [7], $2ZrCl_4 \cdot PCl_5$ [18,19], and $MoCl_4 \cdot 2PCl_5$ [11].

Compounds of PCl_5 with the halides of organic nitrogen bases are also known: $(CH_3)_4NCl \cdot PCl_5 \cdot ICl$ [20], $2C_5H_5N \cdot HCl \cdot PCl_5$ [21]**.

The information on all of these complexes (with the exception of the compounds of PCl_5 with iodine chloride and iodine bromide [15-17] is limited almost exclusively to a brief description of the preparation methods, the external appearance, and at times the melting point or boiling point.

Judging from the few (in a number of cases being contradictory) literature data, these complexes represent substances that are most frequently solid and volatile. They can be purified by sublimation, although some of them decompose when heated, fume in the air, and are decomposed by water.

The physicochemical properties of the complex phosphorus halides, in particular their electrochemical properties, molecular state in solutions and the nature of their ions, have hardly been studied. The same can also be said with respect to the question of the structure of these complexes. Thus, at the same time that A. Werner in his monograph [22] assigned to these complexes the structure $(Cl_4PCl)_m(RClx)_n$, for example $Cl_4PCl \cdot AuCl_3$, Weinland [23]

* Thus, for example, PCl_5 reacts with many unsymmetrical organic compounds, containing either a double or triple bond, in such manner that the PCl_4 group adds to the more hydrogenated carbon atom, while the chlorine atom adds to the less hydrogenated carbon atom [3].

** The preparation of a number of such complexes is also described in the studies of Groeneveld [32].

assigned to the last complex the sharply different structure $\left[Au\begin{matrix}Cl_3\\PCl_5\end{matrix}\right]^-$.

In general, the presence of $[PCl_4]^+$ cations in the complexes of phosphorus pentachloride with the chlorides of other elements was shown only for the complex $[PCl_4]^+ ICl_2^-$ [24], both in solutions [15-17] and in the crystalline state [25].

As regards complexes containing the anion $[PCl_6]^-$, in the literature there fail to exist any convincing proofs for the existence of such complexes. The anion $[PCl_6]^-$ was manifested only in the crystal lattice of phosphorus pentachloride. It is possible that such ions are formed in certain nonaqueous PCl_5 solutions. Thus, phosphorus pentachloride in acetonitrile and nitrobenzene solutions [26] dissociates into ions in accord with the scheme $2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$, which is facilitated by the formation of complexes with the solvent. However, this opinion lacks sufficient experimental support.

Such a state of affairs relative to the question of PCl_5 compounds with metal halides and the undoubted interest that such compounds represent scientifically, (and it is fully possible also in practical respects—for example, for the separation of certain metals [19]), caused us to undertake studies in this field.

These studies were made as follows: at first the corresponding binary systems were studied by several physicochemical analysis methods (thermal analysis, cryoscopy, measurement of electrical conductivity), and also the solutions of these systems in organic solvents, in order to establish the presence and composition of the complexes. Then those complexes, the existence of which was established by physicochemical analysis, were synthesized, and an analytical and physicochemical study of these individual compounds was made. Since these complexes proved to be quite strong electrolytes, attention was directed toward the electrochemical study methods; measurements of the electrical conductivity and study of ionic transfer.

Such a coupling of the physicochemical methods for analyzing the systems with the preparative-analytical method and physicochemical study of the individual compounds permitted us to obtain conclusive data relative to the formation of complexes in the investigated systems, and also data relative to their composition, some of their properties, and their structure.

The present communication is devoted to a study of the process of complex-formation in the system: PCl_5—$AlCl_3$ and PCl_5—$FeCl_3$ in nitrobenzene solutions.

The complexes of PCl_5 with aluminum and iron chlorides were obtained by Weber [6] and Baudrimont [7] by either the fusion of the two chlorides or by the action of PCl_5 on either aluminum or iron, the latter reaction being accompanied by the reduction of part of the PCl_5 to PCl_3.

The formation of the complex $PCl_5 \cdot AlCl_3$ was later confirmed by the thermal analysis of the system PCl_5—$AlCl_3$ [8]. According to the literature data the dystectic, formed in this system, melts at 380°, while the eutectic mixture, containing 33 mole % PCl_5, melts at 25°. According to the data in [7], the melting point of the complex $PCl_5 \cdot AlCl_3$ is 89°.

The thermal analysis results for the systems PCl_5—$AlCl_3$ and PCl_5—$FeCl_3$ were presented earlier; and also the study results for the complexes $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$ [27], obtained in a pure state. The fusion diagrams of these systems are quite similar.

We obtained these complex halides by reacting the original chlorides in a nonaqueous solvent: $PCl_5 \cdot AlCl_3$ — in chloroform, and $PCl_5 \cdot FeCl_3$ — in carbon tetrachloride [27]. The melting points of these complexes (in sealed capillaries) coincided with the values found on the fusion diagrams for the corresponding dystectics. Both complexes show excellent conductivity in nitrobenzene solutions — the specific electrical conductivity at 25 and 45° reaches values of $10^{-3} - 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

In connection with the results of these studies it was of interest to study the process of complex-formation between PCl_5 and $AlCl_3$ or $FeCl_3$ in nonaqueous solvents and to compare such systems with the solutions of the individual complexes.

EXPERIMENTAL

Phosphorus pentachloride, aluminum chloride and ferric chloride were obtained by methods described in the literature [28, 29]. The melting point of phosphorus pentachloride was 160.2° (in sealed test tubes), that of ferric chloride was 302°. The nitrobenzene was purified by the method of Brunner and Galecki [30]. The benzene used

by us was marked "for cryoscopy". All of the preparations were kept in sealed ampuls.

Specific Electrical Conductivity. The electrical conductivity measurements were made by the usual scheme, using a Wheatstone bridge in a vessel equipped with platinized and unplatinized needle electrodes, and making the measurements at 25 and 45°.

The measurement results, obtained with a constant molar ratio of aluminum chloride or ferric chloride to nitrobenzene, but with constantly increasing concentrations of phosphorus pentachloride in the system, are given in Figs. 1 and 2.

The electrical conductivity of these systems increases with increase in the PCl_5 concentration up to an equimolar ratio of PCl_5 to $AlCl_3$ (or $FeCl_3$) and for the investigated concentration ranges it reaches values of $6\text{-}8 \cdot 10^{-3}\ \Omega^{-1}\ cm^{-1}$. Further addition of PCl_5 scarcely changes the electrical conductivity of the given ternary systems, and the specific electrical conductivity isotherms proceed parallel to the abscissa. These facts serve as evidence that complexes showing good conductivity are formed in nitrobenzene solution, which complexes have the composition: PCl_5: $AlCl_3$ and PCl_5: $FeCl_3$ = 1:1.

Since the electrical conductivity of PCl_5 in nitrobenzene is considerably less (by approximately 10 times) than the electrical conductivity of the given complexes in the same solvent, then the appearance of excess PCl_5 molecules in solution fails to exert a noticeable influence on the electrical conductivity properties of the system. The electrical conductivity temperature coefficient is positive.

The specific electrical conductivity for the system PCl_5–$AlCl_3$ (or $FeCl_3$) – $C_6H_5NO_2$ was also measured under the conditions of a constant total molar concentration of the two chlorides and a constant volume. For each experiment the solutions of PCl_5 and the other chloride, each solution having the same molar concentration, were mixed in such volume proportions that the concentration of PCl_5 was gradually increased, and correspondingly the concentration of the $AlCl_3$ or $FeCl_3$ was gradually decreased. The results of these measurements are shown in Figs. 3 and 4.

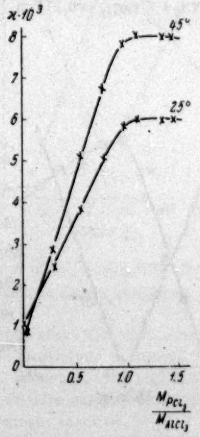

Fig. 1. Specific electrical conductivity of the system $AlCl_3$–PCl_5–$C_6H_5NO_2$. M_{AlCl_3}: $M_{C_6H_5NO_2}$ = 1: 13.7.

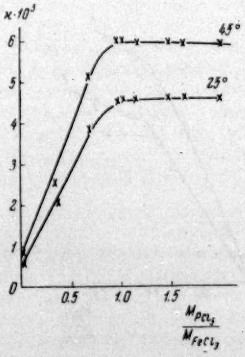

Fig. 2. Specific electrical conductivity of the system PCl_5–$FeCl_3$–$C_6H_5NO_2$. M_{FeCl_3}: $M_{C_6H_5NO_2}$ = 1: 29.0.

With increase in PCl_5 concentration the specific electrical conductivity of the system rises at first until an equimolar ratio of PCl_5 to $AlCl_3$, or correspondingly, to $FeCl_3$, is reached. With further increase in the concentration the specific electrical conductivity for the system decreases. As a result, the specific electrical conductivity curve forms a maximum, passing through the equimolar ratio of both chlprides, in which connection this maximum

fails to shift with temperature change in the interval of 25 to 45°.

Cryoscopic Studies. A study of the electrical conductivity revealed that PCl_5 combines with aluminum and ferric chlorides to form complexes of composition PCl_5: $AlCl_3$ and PCl_5: $FeCl_3$ = 1:1, not only in the binary systems, but also in nitrobenzene solution. For further proof of this conclusion and to determine the composition of the complexes existing in solution the given systems were studied cryoscopically.

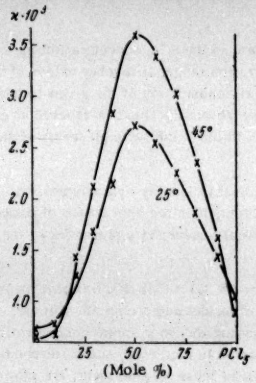

Fig. 3. Specific electrical conductivity of the system $PCl_5-AlCl_3-C_6H_5NO_2$.
$C_{PCl_5} + C_{AlCl_3}$ = 0.4 m.

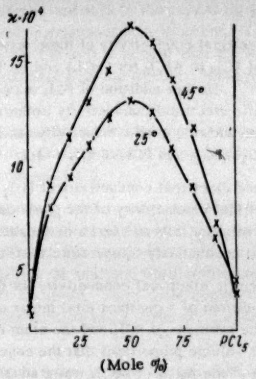

Fig. 4. Specific electrical conductivity of the system. $PCl_5-FeCl_3-C_6H_5NO_2$.
$C_{PCl_5} + C_{FeCl_3}$ = 0.178 m.

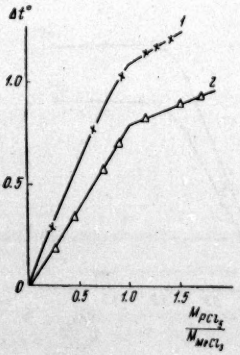

Fig. 5. Cryoscopy of the system $PCl_5-FeCl_3-C_6H_5NO_2$ and $PCl_5-AlCl_3-C_6H_5NO_2$.
1) M_{FeCl_3}: $M_{C_6H_5NO_2}$ = 1 : 82.3, 2) M_{AlCl_3}: $M_{C_6H_5NO_2}$ = 1 : 83.3.

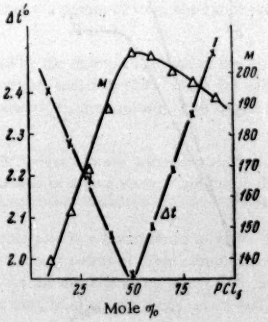

Fig. 6. Cryoscopy of the system $PCl_5-AlCl_3-C_6H_5NO_2$.
$C_{PCl_5} + C_{AlCl_3}$ = 0.4m

The measurements were made by the method proposed by Ya. A. Fialkov and I. D. Muzyka [31]. The results of these investigations are shown in Fig. 5, where the ratios (in moles) of PCl_5 to $AlCl_3$ (or to $FeCl_3$) are plotted along the abscissa, and along the ordinate the change in the depression $\Delta t = \Delta t_1 - \Delta t_0$, where Δt_0 is the freezing

point depression of the starting solution of $AlCl_3$ or $FeCl_3$ in nitrobenzene, and Δt_1 is the depression observed under constantly increasing concentrations of PCl_5.

As can be seen from Fig. 5, the value of Δt rapidly rises to the equimolar proportion of PCl_5 to $AlCl_3$ (or correspondingly to $FeCl_3$), after which the rate of rise is diminished, which can be explained by the weaker electrolytic dissociation of PCl_5 when compared with the complex chlorides that are formed in the given systems.

A cryoscopic study was also made with isomolar solutions having a total chloride concentration of 0.40M for the system $PCl_5-AlCl_3-C_6H_5NO_2$ and 0.18M for the system $PCl_5-FeCl_3-C_6H_5NO_2$; in these experiments the properties chosen were the lowering of the freezing point $\Delta t'$ for the solution when compared with the freezing point of nitrobenzene, and also the "apparent" molecular weight.

The results of these studies revealed (Fig. 6 and 7) that for the equimolar ratio PCl_5: $AlCl_3$($FeCl_3$) the curve depicting the relationship between $\Delta t'$ and the concentration forms a sharp minimum, while on the molecular weight curve a maximum is observed for the same ratio of chlorides.

DISCUSSION OF RESULTS

A physicochemical analysis of the systems $PCl_5-AlCl_3-C_6H_5NO_2$ and $PCl_5-FeCl_3-C_6H_5NO_2$ by the electrical conductivity measurement and cryoscopy methods revealed that PCl_5 forms complexes with aluminum and ferric chlorides in nitrobenzene solution that have the same composition as the complexes that are formed in the corresponding binary systems. The experiments with isomolar solutions gave the same results as were obtained in the experiments where the ratio of $AlCl_3$ or $FeCl_3$ to nitrobenzene was kept constant and the ratio PCl_5: $AlCl_3$ or PCl_5: $FeCl_3$ was varied. But the composition-property diagrams for the systems with isomolar concentrations are characterized by sharper inflections of the curves with a maximum or a minimum*.

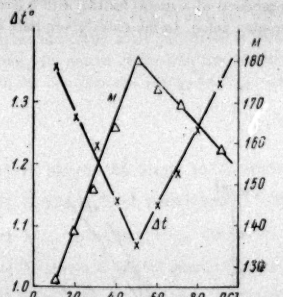

Fig. 7. Cryoscopy of the system $PCl_5-FeCl_3-C_6H_5NO_2$. $C_{PCl_5} + C_{FeCl_3} = 0.18$ m.

The cryoscopic studies permit making a conclusion relative to not only the equimolar ratio of PCl_5 to $AlCl_3$ or $FeCl_3$ in the investigated complexes, but also permit depicting their composition by the formulas $PCl_5 \cdot AlCl_3$ or $PCl_5 \cdot FeCl_3$. According to the cryoscopic measurement data (Figs. 6 and 7) it was possible to calculate the molecular weights of these complexes in nitrobenzene solution as being 207.5 (for $PCl_5 \cdot AlCl_3$) and 180.7 (for $PCl_5 \cdot FeCl_3$). These values proved to be very close to those that were obtained when the molecular weights of the complexes that were synthesized in nitrobenzene were determined by the cryoscopic method. The results of these studies are given in the Table, where the molecular weight values for the complex $PCl_5 \cdot FeCl_3$ in benzene are also indicated** [27].

The data given in the Table show that the molecular weight for these complexes in nitrobenzene rises slightly with increase in concentration, but is reduced by about half when compared with the theoretical values for monomeric forms; this can be explained by the electrolytic or thermal dissociation of the complexes. But the fact that the molecular weight of $PCl_5 \cdot FeCl_3$ in benzene, in the region of small concentrations,*** coincides with the theoretical value, which indicates the relative stability of this type of complex, and also the fairly significant electrical conductivity shown by the nitrobenzene solutions, being of the order of $10^{-3}\ \Omega^{-1}\ cm^{-1}$, give basis to assume that the main reason for the molecular weight reduction of these complexes in nitrobenzene is the dissociation of their molecules into two ions.

*In these experiments there was no need to calculate values for deviation from additivity. Figs. 3, 4, 6 and 7, easily show that curves for such values would have given the same conclusions relative to the composition of complexes as do those based on the curves of corresponding properties.

**The complex $PCl_5 \cdot AlCl_3$ is not soluble in benzene.

***The slight solubility of this complex in benzene prevented studying more highly concentrated solutions.

To characterize the complexes $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$ as electrolytes, in Figs. 8, 9 and 10 are shown the isotherms for the specific and molecular electrical conductivity of these complex chlorides in nitrobenzene solutions. The specific electrical conductivity of $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$ rises rapidly with concentration increase and constitutes for the first of these complexes at a concentration of 0.77M and 25° a value of $6.45 \cdot 10^{-3}\ \Omega^{-1}\ cm^{-1}$ (and at 45° a value of $8.70 \cdot 10^{-3} \Omega^{-1}\ cm^{-1}$), while for $PCl_5 \cdot FeCl_3$ (c= 0.57 m) $5.95 \cdot 10^{-3}$ (25°) and $8.03 \cdot 10^{-3}$ (45°) $\Omega^{-1}\ cm^{-1}$.

The molecular electrical conductivity of these complexes in nitrobenzene solution increases with dilution, i.e. it possesses a "normal" concentration dependence in the investigated concentration interval. Under comparatively slight dilution (v = 113 liters) the electrical conductivity of $PCl_5 \cdot FeCl_3$ in nitrobenzene already attains a value of 81 $\Omega^{-1}\ cm^{-1}$, which is characteristic of binary electrolytes.

Actually, a study of ion transfer in nitrobenzene solutions of $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$ [27] revealed that the cation of these complexes is $[PCl_4]^+$, while the anion is correspondingly either $[AlCl_4]^-$ or $[FeCl_4]^-$.

The study results obtained for the systems $PCl_5 - AlCl_3$ and $PCl_5 - FeCl_3$, and also for their solutions in nitrobenzene and for the nitrobenzene solutions of the complex chlorides $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$, the latter being formed in the given systems, made it possible to characterize these complexes, peculiar in both composition and structure, in greater detail. By means of these studies it was shown that the cation $[PCl_4]^+$, earlier manifested only in the crystal lattice of phosphorus pentachloride and in the complex $PCl_4^+ICl_2^-$, is also contained in the composition of the complexes – the addition products of PCl_5 with the chlorides of aluminum and iron.

The physicochemical, and in particular the electrochemical, properties of these compounds give basis to classify them as being complexes of the binary salt type. In part, a characteristic feature of such complexes consists in the fact that, whereas for the halide salts – the addition products of a metal halide with a nonmetal halide – the nonmetal halide enters into the composition of the complex anion, in the cases given here the nonmetal halide PCl_5 forms the cation of the halide salt.

TABLE

Molecular Weights of the Complexes $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$ *

Concentration (in wt. %)	Depression °C	Molecular Weight
	$PCl_5 \cdot AlCl_3$ in nitrobenzene	
0.52	0.20	179.7
2.50	0.98	180.5
3.26	1.27	183.0
5.48	1.97	203.2
	$PCl_5 \cdot FeCl_3$ in nitrobenzene	
1.35	0.57	165.4
2.65	1.12	170.0
3.62	1.41	184.0
	$PCl_5 \cdot FeCl_3$ in benzene	
0.394	0.055	368.9
0.655	0.09	375.8
0.853	0.12	367.6

* Molecular weight of the complex $PCl_5 \cdot AlCl_3$ = 341.6 of the complex $PCl_5 \cdot FeCl_3$ – 370.7

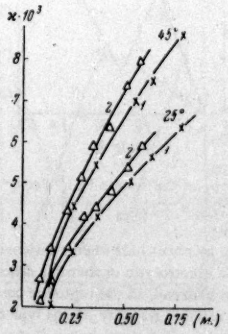

Fig. 8. Specific electrical conductivity of the complexes $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$ in nitrobenzene 1) $AlCl_3 \cdot PCl_5$ 2) $FeCl_3 \cdot PCl_5$.

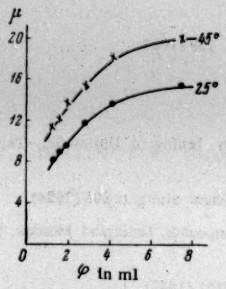

Fig. 9. Molecular electrical conductivity of the system $PCl_5 \cdot AlCl_3 - C_6H_5NO_2$.

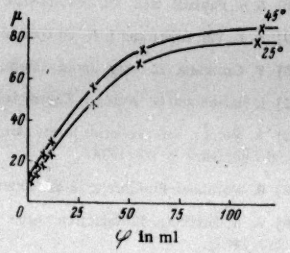

Fig. 10. Molecular electrical conductivity of the system $PCl_5 \cdot FeCl_3 - C_6H_5NO_2$.

SUMMARY

1. A physicochemical analysis of the systems $PCl_5 - AlCl_3 - C_6H_5NO_2$ and $PCl_5 - FeCl_3 - C_6H_5NO_2$ by the electrical conductivity and cryoscopic methods revealed that complex halides, having the composition $PCl_5 \cdot AlCl_3$ and $PCl_5 \cdot FeCl_3$ are formed in them.

2. A comparison of the results obtained in this investigation with the thermal analysis data for the binary systems $PCl_5 - AlCl_3$ and $PCl_5 - FeCl_3$ and with the study results obtained for the above indicated individual complexes in nitrobenzene solutions, made it possible to obtain an idea as to the molecular state of these complexes in solutions, the nature of the ions into which they dissociate, and the nature of their structure as being halide salts with the composition $[PCl_4]^+[AlCl_4]^-$ and $[PCl_4]^+[FeCl_4]^-$.

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DISTINCTIVE CHARACTERISTICS OF ISOMORPHOUS AND ADSORPTION COPRECIPITATION

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For the correct solution of a number of questions associated with coprecipitation it is necessary to know the character of this phenomenon. It is known that coprecipitation can have either an adsorption or an isomorphous character. In both cases the observed phenomena are the same – with the formed precipitate there also coprecipitate other substances, which, taken separately, fail to give a precipitate under these conditions. A number of experimental methods are described in the literature [1-4] for distinguishing between the two types of coprecipitation just mentioned. However, at times it is quite difficult to distinguish between adsorption and isomorphous coprecipitation; for this reason supplementary data on this subject can prove useful.

For distinguishing between the two types of coprecipitation we proposed to study the coprecipitation of variable amounts of the microcomponent with the amounts of the macrocomponent and the other conditions being kept constant, in which number is also included a constant temperature. If here the amount of coprecipitated microcomponent is determined and also its amount, remaining in solution, then it becomes possible to construct the coprecipitation isotherm. Depending on the type of coprecipitation, the latter should possess a variable character.

Adsorption coprecipitation isotherms (i.e. adsorption isotherms) are frequently presented in the literature [6], which isotherms are described by the equation:

$$C_2 = aC_1^{1/n}, \qquad (1)$$

where C_2 is the amount of coprecipitated microcomponent, C_1 is the amount of microcomponent remaining in solution, and a and n are constants.

Graphically, such an isotherm represents a characteristic curve (Fig. 1, Curve 1).

For the case of isomorphous coprecipitation it is possible to construct the corresponding isotherm, which can be named the isomorphous coprecipitation isotherm, proceeding from the known equation of V. G. Khlopin [1]:

$$\frac{x}{a-x} = D\frac{y}{b-y}, \qquad (2)$$

where x is the amount of coprecipitated microcomponent (equal to C_2), a is the initial amount of microcomponent, y is the amount of precipitated macrocomponent, b is the initial amount of macrocomponent, and D is the distribution coefficient.

This means that $a - x$ is the amount of microcomponent remaining in solution (equal to C_1). With a constant amount of the microcomponent and constant precipitation conditions the right-hand side of Equation (2) remains constant. This means that the left-hand side of this equation should also be constant, i.e. the ratio of the coprecipitated amount of the macrocomponent to the amount remaining in the solution fails to change with variation in the initial amounts of the microcomponent. From this it can be concluded that the isomorphous coprecipitation isotherm represents a straight line, passing at a certain angle through the coordinate origin (Figs. 1 and 2).

Our conclusions fail to be changed if the isomorphous coprecipitation proceeds in accord with the so-called logarithmic equation [3, 4, 5, and 7]:

$$\log\frac{a-x}{a} = K\log\frac{b-y}{b}. \qquad (3)$$

Equation (1) can also be written in the logarithmic form:

$$\log C_2 = \log a + \frac{1}{n} \log C_1. \qquad (4)$$

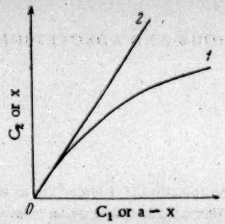

Fig. 1. Scheme of isothermal coprecipitation. 1) adosrption coprecipitation, 2) isomorphous coprecipitation.

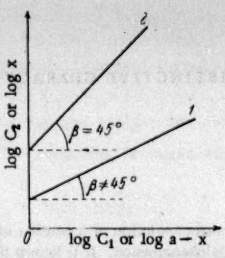

Fig. 2. Scheme of isothermal coprecipitation 1) adsorption coprecipitation 2) isomorphous coprecipitation.

The graph constructed from these data is shown in Fig. 2 (line 1). Since n is usually greater than one, then angle β is less than 45°.

The V. G. Khlopin equation can also be written in logarithmic form:

$$\log x - \log (a - x) = \log D \frac{y}{b - y} \quad . \qquad (5)$$

When working with constant amounts of the macrocomponent and the other conditions being kept constant the right-hand side of the equation proves to be constant, i.e.:

$$\log x - \log (a - x) = \text{const}. \qquad (6)$$

or

$$\log x = \log (a - x) + \text{const}. \qquad (7)$$

The graphical plotting of these data also gives a straight line, but here the ange β is equal to 45° (Fig. 2, 2).

As a result, isomorphous coprecipitation can be distinguished from adsorption coprecipitation by the character of the isotherms.

SUMMARY

A method was proposed for distinguishing between isomorphous and adsorption coprecipitation, the method being based on the different character of the coprecipitation isotherms.

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THE DIPOLE MOMENTS OF INDIUM AND THALLIUM TRIHALIDES

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In their electrochemical properties the halides of trivalent thallium resemble the aluminum halides, being, as is known, homopolar compounds. For example, the homopolar nature of thallium trichloride shows up in the fact that in the molten state it is a poor conductor of electric current; thus, according to the literature [1], the equivalent electrical conductivity of $TlCl_3$ fails to exceed $2.5 \cdot 10^{-5}$ Ω^{-1} cm ^{2}. The homopolar properties of the gallium and indium trihalides are even more definitely manifested. A study of the spatial arrangement of the atoms in the gallium and indium halide molecules revealed that the structure of their double molecules is similar to the structure of the aluminum halides [2].

The aluminum halides have been studied from all sides. The electrical properties of their molecules and the electrochemical behavior in solutions have been studied and the parameters of the molecules in the gaseous state have been determined, which helped to elucidate their structure in considerable degree. The other trihalides of the 3rd group, in particular the compounds of indium and thallium, have been insufficiently studied.

In this paper we studied the dipole moments of indium tribromide and thallium trichloride in dioxane, and also the dipole moments of $TlCl_3$ in benzene and diethyl ether.

The dipole moments were determined by the method of using dilute solutions, for which the dielectric constants and molecular refraction were measured at various concentrations, and also the molecular states of the substances in solution were determined.

The preparation of anhydrous thallium trichloride presents certain difficulties.

Thallium trichloride was first prepared and briefly described by Werther [3], who obtained it by the treatment of metallic thallium or TlCl with chlorine water until complete oxidation had been achieved. The excess chlorine was removed from the solution by evaporation in a vacuum-desiccator in the presence of carbon dioxide until colorless prismatic crystals were obtained. The thallium trichloride monohydrate is obtained after long standing over sulfuric acid in a desiccator. Thallium trichloride was also obtained by the chlorination of thallium chloride with liquid chlorine [4]. In the same paper it was indicated that $TlCl_3$ can also be obtained by the chlorination of a TlCl suspension in either chloroform or in carbon tetrachloride. Our attempts to obtain $TlCl_3$ by the last method failed to give satisfactory results.

According to Meyer [5], thallium chloride, suspended in a small volume of water brought nearly to the boil, is treated with gaseous chlorine. The chlorination is continued until all of the TlCl precipitate has gone into solution and the latter has become completely clear. The solution is then evaporated to a sirupy consistency; on standing of the cooled mixture the thallium trichloride hydrate separates as fine white needles. The anhydrous $TlCl_3$ can be obtained from the hydrate by allowing it to stand in a desiccator over sulfuric acid for 2-3 months. This method for the preparation of anhydrous thallium trichloride, in addition to the length of time required, also suffers from the disadvantage that the $TlCl_3$ is partially decomposed during the dehydration process.

Quite recently [6], in studying different processes for dehydration of a number of metal chlorides, it was found that the use of chlorine in admixture with thionyl chloride for this purpose leads to the formation of anhydrous $TlCl_3$ with a small amount of TlCl (up to 0.2%). The use of phosgene in admixture with chlorine also gives the possibility of obtaining sufficiently pure $TlCl_3$ from thallium chloride. The disadvantage of this method consists in the difficulties of working with phosgene.

EXPERIMENTAL

Since the above indicated methods are inconvenient and are associated with either prolonged dehydration processes or difficulties in operation and do not always assure obtaining a sufficiently pure product we used a different, more rapid and convenient, method for preparing $TlCl_3$. For the indicated purpose a suspension of thallium chloride in water was chlorinated at 60-70° until the suspended solid had disappeared. The solution was then evaporated and the residual water was removed in vacuo with simultaneous passage of chlorine through the solution. The temperature during dehydration was maintained at about 75°. When dehydration was complete the chlorine stream was terminated and the residual chlorine was removed by a passage of a stream of dry air for some time. The thallium trichloride was obtained as a dry, easily sifted white powder.

The obtained compound was analyzed for its chlorine and thallium content. The chlorine was determined by the Volhard method, the thallium having been first precipitated with ammonia. The thallium was determined both gravimetrically and volumetrically.

Thallium trichloride is hydroscopic; it absorbs moisture in the air, forming first the monohydrate, then the tetrahydrate, and on long standing in the air it deliquesces. The contradictory melting point data given in the literature [4-6] are associated with this.

Our observations confirm the data given in [6] that thallium trichloride melts with decomposition in a sealed capillary at 154-156°.

Indium tribromide was obtained by the action of bromine on metallic indium.

The molecular weight of $TlCl_3$ was determined in a hermetically sealed apparatus. Dioxane served as the solvent, the cryoscopic constant of which was taken as equal to 4.70. The determination results are given in Table 1.

The presented data show that thallium trichloride in dioxane is found in the monomolecular state.

The molecular refraction of thallium trichloride was also determined in dioxane. A Pulfrich refractometer was used for making the sodium D-line measurements. A sodium lamp served as the light source. The temperature of the solutions was kept constant at 20 ± 0.01° by means of an ultrathermostat.

TABLE 1

Weight (g)		Amount of $TlCl_3$ (in %)	Δt	Molecular Weight	
Dioxane	$TlCl_3$			Found	Calculated
18.1846	0.3770	2.03	0.315	309	310.76
18.1846	0.5576	2.97	0.465	310	

The study results are given in Table 2, which results show that the molecular refraction of $TlCl_3$ is equal to 29.3 cm^3. The following designations have been adopted in this and subsequent tables: C and P – the molar fraction and polarization of the dissolved substance, and $\underline{n}$, ϵ, and $\underline{d}$ – the index of refraction, dielectric constant and specific gravity of the solution, respectively.

TABLE 2

Molecular Refraction of $TlCl_3$ in Dioxane (λ 589.3 m μ)

Amount of $TlCl_3$ (in %)	C_2	d	n	Molecular Refraction (cm^3)
–	–	1.0336	1.42263	–
5.20	0.01530	1.0791	1.42773	29.3
5.32	0.01567	1.0801	1.42788	29.5
7.28	0.02173	1.0988	1.42999	29.1
8.52	0.02573	1.1100	1.43117	29.4
			Average	29.3

TABLE 3

Dielectric Constants and Polarization of $TlCl_3$ in Benzene at 20°

C_2	d	ϵ	P_2
–	0.8785	2.283	–
0.00054	0.8798	2.295	358
0.00155	0.8824	2.312	300
			$P_{2\infty}$ = 360 cm^3

The dielectric constants of the solutions were determined by the beat method on a wavelength of 301.3 m, for which a heterodyne with quartz stabilizer was used. The measurement results, and also those

calculated from them by the Clausius-Mosotti equation and the rule of mixed polarization values, are given in Tables 3-6.

TABLE 4

Dielectric Constants and Polarization of $TlCl_3$ in Diethyl Ether at 25°

C_2	d	ϵ	P_2
–	0.7089	4.240	–
0.00081	0.7110	4.250	128.1
0.00128	0.7122	4.255	123.9
0.00149	0.7128	4.258	123.5
0.00156	0.7130	4.259	124.1
0.00160	0.7132	4.261	127.3
			$P_{2\infty}$ = 125 cm^3

TABLE 5

Dielectric Constants and Polarization of $TlCl_3$ in Dioxane at 20°

C_2	d	ϵ	P_2
–	1.0329	2.218	–
0.00155	1.0362	2.226	118.6
0.00289	1.0409	2.239	125.0
0.00443	1.0454	2.253	132.3
0.00696	1.0524	2.274	134.2
0.00821	1.0559	2.287	139.9
0.00939	1.0591	2.301	144.9
0.01093	1.0634	2.322	153.8
0.01253	1.0679	2.341	157.3
0.01567	1.0770	2.377	160.1
			$P_{2\infty}$ = 113 cm^3

The equation $P_0 = P_{2\infty} - (P_E + P_A)$, was used to calculate the orientation polarization P_0, where: P_E is the electronic, and P_A the atomic polarization. The electronic polarization was taken as being equal to the molecular refraction, which for the case of $TlCl_3$ in dioxane was determined experimentally, and the same values were taken for the other solvents; for $InBr_3$ the molecular refraction was calculated from the ionic refraction.

The Debye equation was used to calculated the dipole moments: $\mu = 0.0127\sqrt{P_0 T} \cdot 10^{-18}$ electrostatic units.

The dipole moments for $TlCl_3$ and $InBr_3$ in the above mentioned solvents are given in Table 7.

Data on the dipole moments of indium tribromide and thallium trichloride in either the free state or in nonpolar inert solvents fail to exist in the literature, since these compounds are insoluble in such solvents as carbon disulfide, carbon tetrachloride, etc.

TABLE 6

Dielectric Constants and Polarization of $InBr_3$ in Dioxane

C_2	d	ϵ	P_2
–	1.0336	2.218	–
0.00123	1.0374	2.226	118.4
0.00224	1.0407	2.232	112.9
0.00288	1.0427	2.236	113.1
0.00364	1.0450	2.241	114.6
0.00463	1.0481	2.248	116.7
0.00508	1.0495	2.250	114.2
			$P_{2\infty}$ = 115 cm^3

The dipole moment for indium tribromide in dioxane (according to our measurements equal to 1.88 D) can belong, not to the free $InBr_3$ molecule, but instead to the molecular compound of indium tribromide with dioxane, since it has been shown by many examples that dioxane is a strong complexing agent, easily forming compounds with metal halides, which compounds possess high dipole moments.

The same can also be said with respect to $TlCl_3$. From the data in Table 7 it can be seen that thallium trichloride in dioxane, ether, or benzene possesses a dipole moment of some magnitude.

The found values can be inherent either to the moments of thallium trichloride or to the moments of its complexes with the solvents in which the measurements were run. The first postulation possesses small probability, since different values for the dipole moments are found in different solvents.

TABLE 7

Polarization and Dipole Moments of $InBr_3$ and $TlCl_3$

Compound	$P_{2\infty}$	P_E	P_{E+A}	P_0	$\mu \cdot 10^{18}$
$InBr_3$ in dioxane	115	35.3	40	75	1.88
$TlCl_3$ in dioxane	113	29.3	34	79	1.93
$TlCl_3$ in diethyl ether	125	29.3	34	91	2.04
$TlCl_3$ in benzene	360	29.3	34	326	3.93

The second postulation that polar compounds of thallium trichloride with the solvents are formed seems more valid to us. The formation of the thallium trichloride complex with diethyl ether, namely $TlCl_3 \cdot (C_2H_5)_2O$, which complex is described in the literature [5], can serve in support of this.

Thallium trichloride with dioxane forms the compound $TlCl_3 \cdot 2C_4H_8O_2$, isolated by us in the crystalline state. Here it should be mentioned that $TlCl_3$ apparently forms at least two compounds with dioxane, of which one shows greater stability in concentrated solutions. This can be seen from the data in Table 5, showing that the dielectric polarization decreases with reduction in the $TlCl_3$ concentration, whereas for most substances it is customary for the dielectric polarization to increase with dilution. We were unable to isolate the compound of thallium trichloride with benzene. However, the presence of a large dipole moment is characteristic for this system, analogous to the situation observed for aluminum bromide in benzene, for which a dipole moment of 5.09 D [7] was found and proved by the method of thermal analysis for the presence of the compound $AlBr_3 \cdot C_6H_6$ [8]. In other solvents (bromine, carbon disulfide, cyclohexane), where reaction with aluminum bromide is absent, the dipole moment is equal to zero.

The greater dielectric polarization of $TlCl_3$ solutions in benzene can serve as an indication that thallium trichloride reacts with benzene to form the transient compound $TlCl_3 \cdot nC_6H_6$, and, as a result, the measured dipole moment belongs to this complex.

SUMMARY

1. The dipole moment of indium tribromide in dioxane was determined as being μ = 1.88 D.

2. The dipole moments of thallium trichloride were determined in dioxane (μ = 1.93 D), in diethyl ether (μ = 2.04 D), and in benzene (μ = 3.93 D).

3. It was postulated that the greater values for the dipole moments of $InBr_3$ and $TlCl_3$ in these solvents are due to the formation in solution of molecular compounds between the indium and thallium trihalides and the solvents.

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COMPLEX-FORMATION AND EXCHANGE DECOMPOSITION IN THE RECIPROCAL SYSTEM OF SODIUM AND CADMIUM CHLORIDES AND SULFATES

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Among inorganic salts the sulfates are distinguished by a great tendency for complex-formation, both in aqueous solutions and in melts. A study of reciprocal system melts, especially with participation of the more easily fusible salts [1], makes it possible to follow the interrelationships of sulfates and also to develop in a wide temperature interval the interrelationships that prevail between complex-formation and exchange decomposition. The cadmium salts are of interest for the reason that they show a great tendency to form autocomplexes, which is especially well manifested for the halides, in particular for CdI_2, and also to form complexes with the alkali metal salts.

Of the elements of the secondary subgroup of Group II the following reciprocal systems have been studied up to the present time: Li, Zn ‖ Cl, SO_4 [2], Na, Zn ‖ Cl, SO_4 [3], K, Zn ‖ Cl, SO_4 [4], and also Li, Cd ‖ Cl, SO_4 [5].

Of the element of the main subgroup of Group II the following reciprocal systems have already been studied: Na, Mg ‖ Cl, SO_4 [6], K, Mg ‖ Cl, SO_4 [7].

The greatest tendency for complex-formation was revealed for the systems in which Mg, Zn or Cd participated, and also for the system K, Ca ‖ Cl, SO_4 [8]. The formation of hetero compounds of the kainite type was established only in the systems K, Mg ‖ Cl, SO_4 and K, Zn ‖ Cl, SO_4. The formation of internal hetero compounds fails to be observed for all of the other enumerated systems.

In this communication we present our investigation results on a reversible-reciprocal adiagonal system with subordinate diagonal of sodium and cadmium chlorides and sulfates.

EXPERIMENTAL

Method of Operation and Substances. The study was made by the visual-polythermal method, using a platinum crucible and a shaft furnace; a Pt, Rh/Au, Pd, Pt thermocouple with a sensitive millivoltmeter and mirror scale was used. In view of the volatile nature of $CdCl_2$ (m.p. 568°, b.p. 960°) we avoided overheating the melts; after a certain number of additions had been made the batch was renewed again, and in that way the constants of the previous melt were verified. The preparation, purification and dehydration of the cadmium salts should be done with especial care so as to avoid the appearance of a fine suspension or of the brown hydrolysis product, namely CdO, both of which interfere with the visual determinations. Our melts were completely clear.

All of the compositions are given in equimolar percents.

Constants of the Substances. Melting points: NaCl 800°, Na_2SO_4 884°, $CdCl_2$ 568°, $CdSO_4$ ~ 1000° ($CdSO_4$ suffers slight decomposition when fused and consequently its melting point is not distinct). Na_2SO_4, for which only its polymorphous transformation at 236-240° is accurately determined, according to our data, also shows homomorphous transformation at 758° and the polymorphous transformations at 604 and 550°. *

The conditional heat effect of the exchange reaction $Na_2Cl_2 + CdSO_4 \rightleftharpoons Na_2SO_4 + CdCl_2$ is equal to 3.225 kcal / equiv. in the direction of the sulfate of the monovalent metal and the chloride of the divalent metal.

Binary Systems. 1. Na_2Cl_2–Na_2SO_4. Has a eutectic at 65% Na_2SO_4 and 628° [6]. According to our data, homomorphous transformation on the branch occurs at 758° and 17% Na_2Cl_2 (Fig. 1, Table 1).

* For brevity's sake we omitted some of the sections, and also a number of points in the tables.

2. $CdCl_2$–$CdSO_4$. Has a eutectic at 540° and 15% $CdSO_4$ [9]. In view of the volatile nature of $CdCl_2$ we studied the curve only up to 35% $CdSO_4$ and 700° (Fig. 1, Table 1).

3. Na_2Cl_2–$CdCl_2$ [10]. This system has the compound $2NaCl \cdot CdCl_2$, which melts with decomposition. The eutectic point is at 387° and 29% Na_2Cl_2; the transition point at 433° and 38% Na_2Cl_2 (Fig. 1, Table 1).

4. Na_2SO_4–$CdSO_4$. According to the data of [11], the compound $Na_2SO_4 \cdot 3CdSO_4$, melting with decomposition, appears on the diagram.

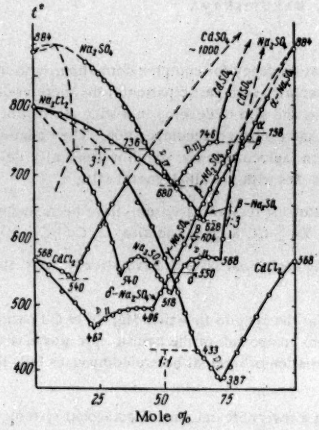

Fig. 1. Sides and diagonal sections of the reciprocal system Na, Cd || Cl, SO_4.

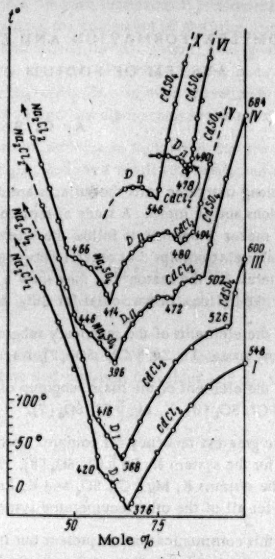

Fig. 2. Internal sections of the system: I, III, IV, V, VI, X.

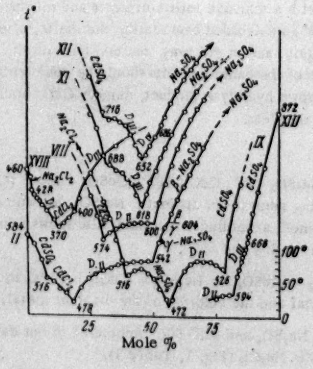

Fig. 3. Internal sections of the system: II, VIII, IX, XI, XII, XIII, XVIII.

The eutectic point is at 681° and 46% Na_2SO_4, and the transition point at 746° and 30% Na_2SO_4. The authors indicate polymorphous transformation in the solid state for the compound 1:3 at 456°, and also the formation in the solid state of compound 1:1 at 551° and of 3:1 at 351°. In addition, individual transformations are shown on their diagram, which transformations are not correlated with the general structure of the diagram. According to our data a supplementary transformation is established on the Na_2SO_4 branch at 736° and 43.5% $CdSO_4$, which, apparently corresponds to the compound $3Na_2SO_4 \cdot CdSO_4$ (Fig. 1, Table 1). Inside the reciprocal system (Figs. 5 and 6) this branch corresponds to a small field, merging into the transition point R_1 at 640°. The obtained data raise the question of the need for complete revision of the constitution diagram of this binary system in the solidus region, since the long field of the compound $Na_2SO_4 \cdot CdSO_4$ begins at 610° in the melts of

the reciprocal system. In reference [11] it is indicated that this compound begins to form at 551° *.

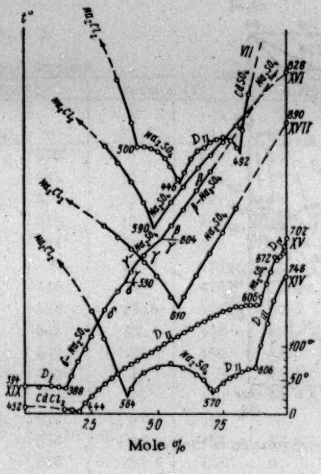

Fig. 4. Internal sections of the system: VII, XIV, XV, XVI, XVII, XIX.

Diagonal Sections. 1. Triangulation Section $CdCl_2-Na_2SO_4$. The three main crystallization branches intersect at 462° and 22.5% and 496° and 45.5% Na_2SO_4. On the Na_2SO_4 branch intersection of the curves is observed at 550° and 52.5%, 604° and 59% Na_2SO_4. The main middle branch corresponds to the crystallization of $Na_2SO_4 \cdot CdSO_4$ (Fig. 1, Table 1). This diagonal fails to have the character of a binary system, but nevertheless it is a triangulating section (Fig. 5).

2. Metastable Section $Na_2Cl_2-CdSO_4$. The main branches intersect at 540° and 33.5%, 518° and 52% and 568° and 71.5% $CdSO_4$ (Fig. 1, Table 1). It intersects all four phase triangles of the reciprocal system composition square.

Adiagonal Triangulation Section. $CdCl_2-Na_2SO_4 \cdot CdSO_4$ has a eutectic point with inversion at 480° and 18% Na_2Cl_2, which point corresponds to the maximum temperature for the internal stable nonvariant points. We will mention that in the evirons of the $Na_2SO_4-CdSO_4$ side on this section the compound $3Na_2SO_4 \cdot CdSO_4$ separates at first, and is already decomposed at 640° (Fig. 5).

TABLE 1

Binary Systems and Diagonal Sections

$Na_2Cl_2-Na_2SO_4$		$Na_2Cl_2-CdCl_2$		$CdCl_2-CdSO_4$		$Na_2SO_4-CdSO_4$		$CdCl_2-Na_2SO_4$		$Na_2Cl_2-CdSO_4$	
% Na_2SO_4	t	% Na_2Cl_2	t	% $CdSO_4$	t	% $CdSO_4$	t	% Na_2SO_4	t	% $CdSO_4$	t
0	800°	0	568°	0	568°	0	884°	0	568°	0	800°
10	790	5	546	5	560	20	868	5	548	17.5	708
25	760	10	518	10	550	27.5	840	15	504	25	652
40	722	15	486	12.5	546	35	800	21	473	30	596
50	694	20	452	15	540	37.5	780	24	472	32.5	554
55	676	22.5	432	17.5	564	40	766	27	480	35	560
57.5	664	25	410	20	584	42.5	746	33	490	40	574
60	654	27.5	394	25	620	45	730	39	496	42.5	570
62.5	638	30	394	30	652	47.5	716	45	496	47.5	546
65	628	32.5	408	35	684	50	702	48	518	50	528
67.5	654	35	422			52.5	688	51	544	52	520
72.5	690	37.5	432			55	686	55	570	55	538
77.5	724	40	460			57.5	702	57.5	592	61	570
80.	740	42.5	490			62.5	724	60	610	64	574
82.5	752	45	520			67.5	746	62.5	632	67	572
85	774	50	572			70	746	67.5	674	70	570
87.5	794	55	618			72.5	784	72.5	714	72.5	600
90	810	60	656			75	818	75	732	80	750

* For brevity's sake in the future we will designate the formulas of the complexes by: $D_I - 2NaCl \cdot CdCl_2$, $D_{II} - Na_2SO_4 \cdot CdSO_4$, $D_{III} - Na_2SO_4 \cdot 3CdSO_4$ and $D_{IV} - 3Na_2SO_4 \cdot CdSO_4$.

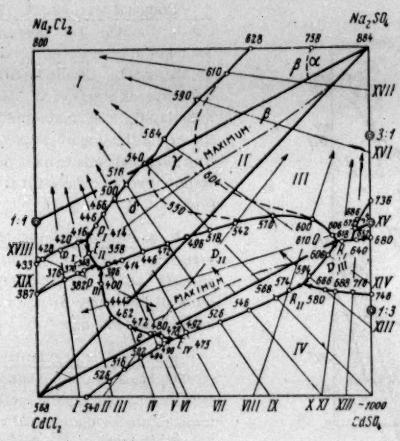

Fig. 5. Distribution of the internal sections and triangulation of the system: Na, Cd ‖ Cl, SO_4.

Reciprocal System

A total of 19 internal sections was studied (Figs. 2-5, Tables 2 and 3).

The temperatures and compositions of the intersection points for the curves in the sections are given in the summary Table 4.

The surface of crystallization for the system (Figs. 5 and 6) consists of 8 main crystallization fields of which the Na_2SO_4 field is further subdivided into the fields of α-, β-, γ- and δ-modifications. The dimensions of the fields with respect to the area of the composition square are (in %): Na_2Cl_2 21.92, $CdCl_2$ 8.61, $CdSO_4$ 17.36, Na_2SO_4 32.65, $2NaCl \cdot CdCl_2$ 1.48, $Na_2SO_4 \cdot CdSO_4$ 15.5, $Na_2SO_4 \cdot 3CdSO_4$ 2.1, $3Na_2SO_4 \cdot CdSO_4$ 0.38.

The crystallization fields converge into 7 nonvariant points, of which R_I, R_{II} and Q correspond to the equilibria of the solid phases of one of the sides, namely $Na_2SO_4-CdSO_4$, and consequently they fail to participate in the triangulation (Table 5).

The reciprocal system Na, Cd ‖ Cl, SO_4 is divided by the three triangulation sections $Na_2Cl_2 \cdot CdCl_2-Na_2SO_4$, $CdCl_2-Na_2SO_4$ and $CdCl_2-Na_2SO_4 \cdot CdSO_4$ into the four phase triangles (Fig. 5): I) $Na_2Cl_2 \cdot CdCl_2-Na_2Cl_2-Na_2SO_4$, II) $Na_2Cl_2 \cdot CdCl_2-Na_2SO_4-CdCl_2$, III) $CdCl_2-Na_2SO_4-Na_2SO_4 \cdot CdSO_4$, IV) $CdCl_2-Na_2SO_4 \cdot CdSO_4-CdSO_4$.

The chemistry of the reactions proceeding in the system can be represented by the equations:

$$2Na_2Cl_2 + CdSO_4 = Na_2Cl_2 \cdot CdCl_2 + Na_2SO_4,$$
$$Na_2Cl_2 + CdSO_4 = CdCl_2 + Na_2SO_4,$$
$$Na_2Cl_2 + 2CdSO_4 = CdCl_2 + Na_2SO_4 \cdot CdSO_4.$$

The last reaction appears as the most characteristic in the system, and consequently on the triangulation section $CdCl_2-Na_2SO_4 \cdot CdSO_4$ we have a single eutectic point with inversion in the system at 480° and 18% Na_2Cl_2, which, as was indicated above, appears as the maximum temperature with respect to the stable nonvariant points P_I, E_{II}, P_{III}, and E_{IV}. As a result of this, the system should be regarded as belonging to the adiagonal type with subordinate diagonal.

The most interesting feature of the studied reciprocal system is the decomposition on cooling of both of the

compounds with compositions 3 : 1 and 1 : 3 of the Na_2SO_4–$CdSO_4$ side, and the extreme stability of the sharply defined $Na_2SO_4 \cdot CdSO_4$ complex.

TABLE 2

Internal Sections

Section II		Section IV		Section VII		Section IX		Section XIV		Section XV	
% Na_2SO_4	t	% Na_2Cl_2	t	% Na_2Cl_2	t	% Na_2Cl_2	t	% Na_2Cl_2	t	20% Na_2Cl_2 80% $CdCl_2$	t
2.5	570°	5	610°	15	580°	15	656°	5	710°	1	690°
5	545	10	536	17.5	528	20	582	10	642	2	680
7.5	517	13	497	20	504	22.5	528	12.5	610	3	675
10	513	17.5	492	22.5	516	25	534	15	604	4	673
15	494	20	482	25	518	30	540	17.5	600	4.5	675
18	482	22.5	476	27.5	514	35	536	22.5	592	6	654
24	518	25	476	32.5	502	40	506	27.5	576	10	616
30	528	27.5	466	37.5	484	42.5	480	30	576	12	604
42	542	32.5	446	40	466	45	482	32.5	590	16	602
48	542	37.5	400	42.5	454	50	514	40	406	22.5	596
52.5	570	40	410	45	474	55	528	45	612	32.5	578
55	594	45	432	50	496	57.5	526	55	598	45	550
57.5	612	47.5	440	55	502	60	520	60	570	60	512
60	636	50	454	57.5	504	62.5	540	65	600	77.5	456
65	676	52.5	486	60	538	67.5	605	70	652	80	444
70	718	60	578	65	600	70	632	75	694	85	446

TABLE 3

Internal Sections

Section III		Section VI		Section XI		Section XII		Section XIII		Section XIX	
% Na_2Cl_2	t	% Na_2Cl_2	t	% Na_2SO_4	t	% Na_2SO_4	t	% Na_2Cl_2	t	% Na_2SO_4	t
2.5	560°	10	614°	25	762°	25	780°	5	790°	10	390°
5	524	12.5	564	27.5	742	27.5	752	7.5	752	15	388
10	514	14	544	30	694	30	724	10	718	17.5	406
20	482	14.5	520	32.5	684	32.5	716	12	690	22.5	446
25	450	15.5	496	35	676	39	704	12.5	684	30	506
30	410	16	492	39	664	43	673	13.5	664	35	534
35	372	16.5	486	43	636	45	658	14.5	652	40	560
37.5	382	17	484	45	624	47	658	15	646	45	582
40	394	17.5	494	47.5	640	49	674	16	632	50	602
42.5	410	18	496	51	674	51	684	17	622	55	628
45	440	20	498	57.5	730	53	704	20	592	60	654
55	570	22.5	502	62.5	766	57	736	22.5	592	65	682
60	620	25	502	67.5	798	70	816	25	590	70	710

An interesting type of crystallization surface is depicted in relief by the isotherms inside the crystallization fields of the reciprocal system (Fig. 6). Two projections were drawn to make the details of the crystallization surface more exact, of which the one on the $CdSO_4$–Na_2SO_4 side is shown in Fig. 7, while the crystallization tree diagram is shown in Fig. 8.

Ridges appear in the Na_2SO_4 fields and the $Na_2SO_4 \cdot CdSO_4$ complex, being depicted by the maxima curves and inclined away from the corresponding triangulation sections. In contrast to the system Na, Zn || Cl, SO_4, the internal ternary compound, melting with decomposition, is absent in our system.

TABLE 4

Section No.	Fig. Nos.	Starting mixture of components	Melting point of starting mixture	Component or mixture of components added	Intersection of crystallization curves							
					I and II		II and III		III and IV		III and IV	
					A *	t	A	t	A	t	A	t
I	2	87.5% $CdCl_2$ + 12.5% $CdSO_4$	546°	Na_2Cl_2	33	376°	42	420°	—	—	—	—
II	3	80% $CdCl_2$ + 20% $CdSO_4$	584	Na_2SO_4	7.5	516	18	478	50	542°	56.5	604°
III	2	77.5% $CdCl_2$ + 22.5% $CdSO_4$	600	Na_2Cl_2	4	526	36	368	44	416	—	—
IV	2	65% $CdCl_2$ + 35% $CdSO_4$	684	Na_2Cl_2	11	502	20	472	38	396	49	446
V	2	57.5% $CdCl_2$ + 42.5% $CdSO_4$	(724) **	Na_2Cl_2	14	494	18	480	39	414	52.5	466
VI	2	55% $CdCl_2$ + 45% $CdSO_4$	(740)	Na_2Cl_2	15	490	17	478	—	—	—	—
VII	4	45% $CdCl_2$ + 55% $CdSO_4$	(792)	Na_2Cl_2	18.5	492	41.5	446	57	500	—	—
VIII	3	35% $CdCl_2$ + 65% $CdSO_4$	(842)	Na_2SO_4	30.5	574	51	600	—	—	—	—
IX	3	30% $CdCl_2$ + 70% $CdSO_4$	(866)	Na_2Cl_2	21.5	526	43.5	472	61	516	—	—
X	2	15% $CdCl_2$ + 85% $CdSO_4$	(936)	Na_2Cl_2	25	546	—	—	—	—	—	—
XI	3	15% $CdCl_2$ + 85% $CdSO_4$	(936)	Na_2SO_4	31	688	45	618	—	—	—	—
XII	3	7.5% $CdCl_2$ + 92.5% $CdSO_4$	(970)	Na_2SO_4	30.5	716	45.5	652	51.5	686	—	—
XIII	3	20% Na_2SO_4 + 80% $CdSO_4$	872	Na_2Cl_2	13	666	18.5	594	—	—	—	—
XIV	4	32.5% Na_2SO_4 + 67.5% $CdSO_4$	746	Na_2Cl_2	12.5	606	29	570	61	564	—	—
XV	4	50% Na_2SO_4 + 50% $CdSO_4$	702	20% Na_2Cl_2 + + 80% $CdCl_2$	4.5	672	11	606	21	444	—	—
XVI	4	70% Na_2SO_4 + 30% $CdSO_4$	828	Na_2Cl_2	51.5	590	—	—	—	—	—	—
XVII	4	87.5% Na_2SO_4 + 12.5% $CdSO_4$	(890)	Na_2Cl_2	57.5	610	—	—	—	—	—	—
XVIII	3	40% Na_2SO_4 + 60% $CdCl_2$	460	$CdSO_4$	1.5	428	12.5	370	19.5	400	—	—
XIX	4	30% Na_2Cl_2 + 70% $CdCl_2$	394	Na_2SO_4	16	388	38.5	550	51	604	—	—

* A- percent of added component.

** The temperature given in parentheses were obtained by interpolation.

TABLE 5

Nature of the Point	t	Composition (in Mole %)				Equilibrium Phases
		Na_2Cl_2	$CdSO_4$	Na_2SO_4	$CdCl_2$	
Transition P_I	414°	44.5	15.5	–	40	Na_2Cl_2, δ-Na_2SO_4, D_I
Eutectic E_{II}	358	37.5	18.5	–	44	$CdCl_2$, D_I, δ-Na_2SO_4
Transition P_{III}	382	36.5	19	–	44.5	$CdCl_2$, δ-Na_2SO_4, D_{II}
Eutectic E_{IV}	475	17	41.5	–	41.5	$CdCl_2$, $CdSO_4$, D_{II}
Cross R_I	640	5.5	49	45.5	–	D_{IV}, D_{III}, β-Na_2SO_4
Cross R_{II}	580	20.5	47	32.5	–	D_{III}, D_{II}, $CdSO_4$
Point of phase Q appearance	610	9.5	45.5	45	–	β-Na_2SO_4, D_{II}, D_{III}

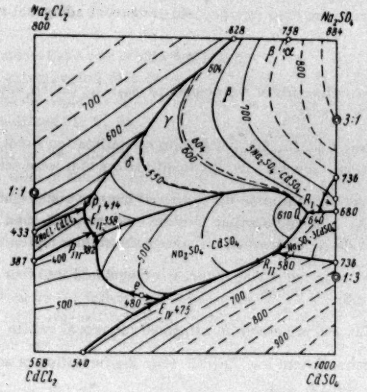

Fig. 6 Projection of the three-dimensional diagram of the reciprocal system Na, Cd || Cl, SO_4 on the composition square.

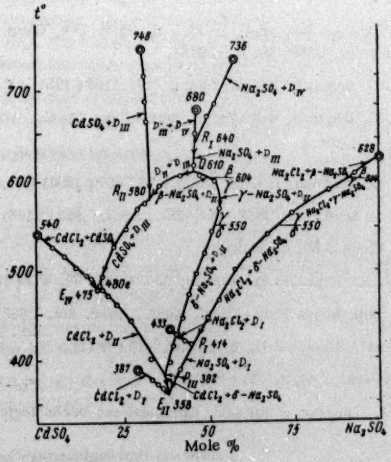

Fig. 7. Projection of the mutual crystallization curves on the polytherm plane of the binary system $CdSO_4$–Na_2SO_4.

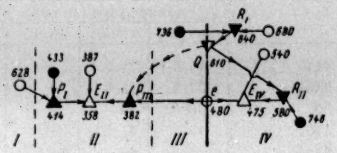

Fig. 8. Diagram of the crystallization tree for the reciprocal system Na, Cd || Cl, SO_4.

In its general character the reciprocal system Na, Cd || Cl, SO_4 resembles the system Na, Pb || Cl, SO_4 [12]; this reciprocal system belongs to the class of reversible-reciprocal adiagonal systems.

SUMMARY

1. A new branch for the crystallization of the compound $Na_2SO_4-CdSO_4$ was established on the fusion curve in the binary system $3Na_2SO_4 \cdot CdSO_4$.

2. The reciprocal system Na, Cd || Cl, SO_4 has 8 main crystallization fields, of which the Na_2SO_4 field is further subdivided into four portions, occupied by the modifications that were established by us.

3. As the result of the decomposition inside the system of the two compounds with compositions 3 : 1 and 1 : 3, found on the $Na_2SO_4-CdSO_4$ side and merging into the cross points R_I and R_{II}, there appears an internal crystallization field for $Na_2SO_4 \cdot CdSO_4$, formed on the side in the solidus region.

4. The composition square of the reciprocal system is triangulated into four phase triangles, the nonvariant points of which are given in Table 5.

5. The system Na, Cd || Cl, SO_4 represents an adiagonal reciprocal system with subordinate diagonal.

6. In contrast to the reciprocal system Na, Zn || Cl, SO_4, the formation of an internal ternary hetero compound is absent in the system Na, Cd || Cl, SO_4.

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FUSION DIAGRAMS OF THE TERNARY SYSTEMS: POTASSIUM NITRATE-CHLORIDE-BROMIDE AND SILVER NITRATE-CHLORIDE-BROMIDE

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The studied ternary systems have one of the binary sides being characterized by a continuous series of solid solutions. The accumulated experimental data on ternary systems establishes the interrelationship that exists between the third component and the stability of the continuous solid solutions, which under its influence can either suffer decomposition or be stabilized [1, 2, 3].

In the systems studied by us the stability of the solid solutions is retained; here we observed that if single-type complexes are formed on the sides of the isotherm triangle of the ternary system, adjacent to one of angles, and the corresponding components give a continuous series of solid solutions, that we will then have complete isomorphism of both compounds. The liquidus surface of similar systems is composed of three crystallization fields: 1) continuous solid solutions of the two components, 2) continuous solid solutions of the isomorphous compounds, and 3) third component.

The above can be verified by the following examples of ternary systems, possessing isomorphous compounds: 1) Sr, K, Ba$\|$Cl [4]$-2KCl \cdot SrCl_2$ and $2KCl \cdot BaCl_2$, 2) Na, K, Ca$\|$ CO_3 [4] $-Na_2CO_3$ $CaCO_3$ and $K_2CO_3 \cdot CaCO_3$, 3) K$\|$$NO_3$, Cl, Br$-KNO_3 \cdot KCl$ and $KNO_3 \cdot KBr$, 4) Ag$\|$$NO_3$, Cl, Br$-AgNO_3 \cdot AgCl$ and $AgNO_3 \cdot AgBr$.

EXPERIMENTAL

The ternary systems of potassium nitrate, chloride and bromide and of silver nitrate, chloride and bromide were studied by the visual-polythermal method. The mixtures were melted in glass test tubes, with stirring by a glass stirrer. A nichrome-constantan thermocouple was used to record the temperature of first appearance of crystals. The salts KNO_3, KCl, KBr and $AgNO_3$ were recrystallized from commercial c. p. reagents, while the AgCl and AgBr were synthesized from the recrystallized $AgNO_3$, KCl and KBr.

The melting points of the pure components were: KNO_3 337°, KCl 774° KBr 740°, $AgNO_3$ 208°, AgCl 452° and AgBr 419°.

Molar percents are indicated in all cases.

Binary Systems *.

1. The System KNO_3-KCl was studied earlier [4, 5, 6]; it has a eutectic point at 320° and 6% KCl and a transition point at 360° and 17.4% KCl, corresponding to the compound $KNO_3 \cdot KCl$ melting with decomposition.

2. The System KNO_3-KBr was studied earlier [6]; it has a eutectic point at 336° and ~ 0.7% KBr and a transition point at 342° and 4.5% KBr, corresponding to the compound $KNO_3 \cdot KBr$ melting with decomposition.

3. The System KCl−KBr was studied by many authors [5, 7]. Continuous solid solutions are formed in it with a minimum at 734° and 40% KCl.

4. The System $AgNO_3-AgCl$ was studied earlier [5, 6]; it is characterized by a eutectic point at 176° and 18.5% AgCl and a transition point at 200° and 31% AgCl, corresponding to the compound $AgNO_3 \cdot AgCl$, melting

* All of the binary systems were repeated by us.

with decomposition.

5. The System $AgNO_3-AgBr$ was studied earlier [5]; it has a eutectic point at 155° and 76% $AgNO_3$ and a transition point at 188° and 54.5% $AgNO_3$, corresponding to the compound $AgNO_3 \cdot AgBr$.

6. The System AgCl–AgBr was studied by a number of authors [5, 6]; it gives a continuous series of solid solutions with a minimum at 415.5° and 74.1% AgBr.

Ternary System $KNO_3 - KCl - KBr$

A total of 9 internal sections was drawn, a brief characterization of which is given in Table 1 (Figs. 1 and 2).

TABLE 1

Section No.	Starting mixture	Melting point of starting mixture	Component added	Intersection points of the crystallization branches		Crystallization branches*	Figure No.
				(%)	Temperature		
1	97% KNO_3 + 3% KCl	328°	KBr	0.8	326°	I and II	1
				4.5	342	II and III	
2	95% KNO_3 + 5% KCl	323		0.5	322	I and II	1
				4.5	344	II and III	
3	90% KNO_3 + 10% KCl	336		2.8	348	II and III	1
4	85% KNO_3 + 15% KCl	354		0.7	356	II and III	1
5	81.5% KNO_3 + 18.5% KCl	375		–	–	III	1
6	95% KNO_3 + 5% KBr	345	KCl	–	–	III	2
7	90% KNO_3 + 10% KBr	387		–	–	III	2
8	85% KNO_3 + 15% KBr	420		–	–	III	2
9	80% KNO_3 + 20% KBr	451		–	–	III	2

The liquidus surface of the ternary system $K\|NO_3$, Cl, Br (Fig. 3) is divided by the two lines of mutual crystallization, without minimum, into three crystallization fields: 1) continuous solid solutions of potassium chloride and bromide, 2) continuous solid solutions of compounds, melting with decomposition, of the anionic complex ($KNO_3 \cdot KCl + KNO_3 \cdot KBr$), 3) potassium nitrate. Their respective areas in percents of the total area of the triangle are: solid solutions K(Cl, Br) – 99.03, solid solutions of the compounds – 0.8, and KNO_3 – 0.17.

Ternary System $AgNO_3 - AgCl - AgBr$

This system was studied with the aid of 8 internal sections through the vertexes and 2 parallel sides of the AgCl–AgBr triangle (Table 2, Figs. 4 and 5).

The form and character of the diagram for the ternary system $AgNO_3-AgCl-AgBr$ (Fig. 6) is analogous to the diagram for the ternary system $KNO_3-KCl-KBr$. The substitution of Ag^+ for K^+ fails to introduce any essential changes.

The liquidus surface of the ternary system $Ag\|NO_3$, Cl, Br is characterized by three crystallization fields; 1) continuous solid solutions of silver chloride and bromide, 2) continuous solid solutions of compounds, melting with decomposition, of the anionic complex ($AgNO_3 \cdot AgCl + AgNO_3 \cdot AgBr$), and 3) silver nitrate. Their respective areas in percents of the total area of the triangle are: solid solutions Ag(Cl, Br) 83.7, solid solutions of the compounds 11.93, and $AgNO_3$ 4.37.

The line for the polymorphous transformations of silver nitrate crosses the $AgNO_3$ crystallization field at 159°. The extremes fail to be characterized by mutual crystallization lines.

*I – KNO_3, II – solid solutions $KNO_3 \cdot KCl + KNO_3 \cdot KBr$, III – solid solutions K(Cl, Br).

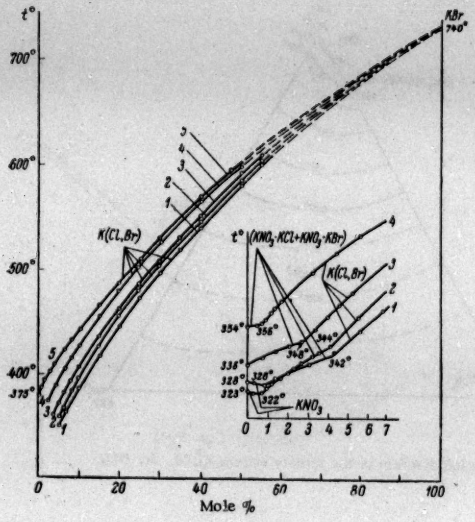

Fig. 1. Internal sections through the system K‖Cl, Br, NO_3.
1-5—Section Numbers (Table 1).

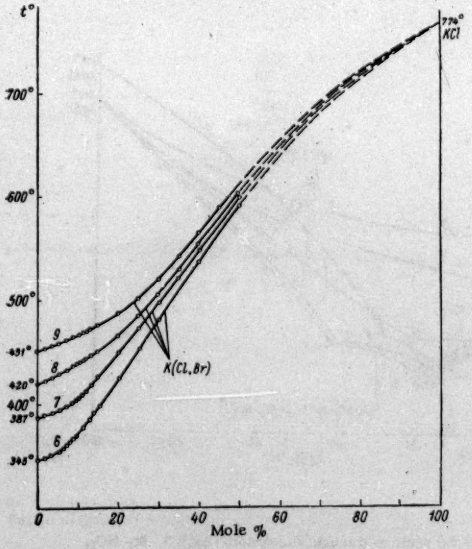

Fig. 2. Internal sections through the system K‖Cl, Br, NO_3.
6-9—Section Numbers (Table 1).

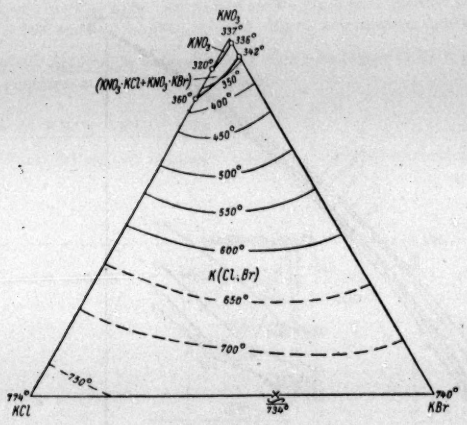

Fig. 3. Fusion diagram of the ternary system K||Cl, Br, NO_3.

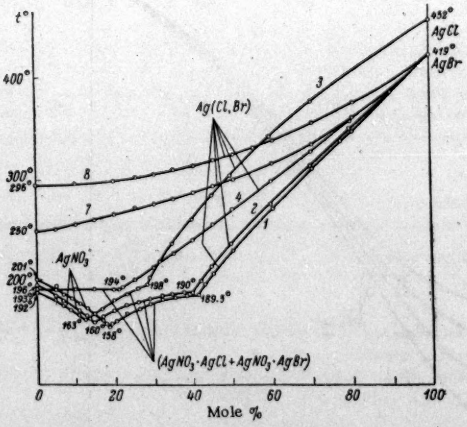

Fig. 4. Internal sections throught the system Ag||Cl, Br, NO_3. 1-4, 7, 8--Section Numbers (Table 2).

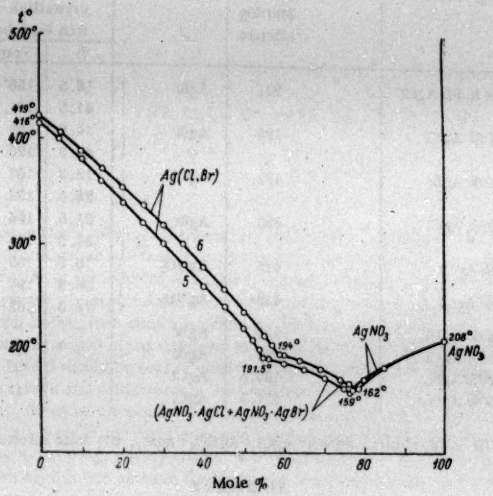

Fig. 5. Internal sections on the AgCl–AgBr side. 5 and 6-Section Numbers (Table 2).

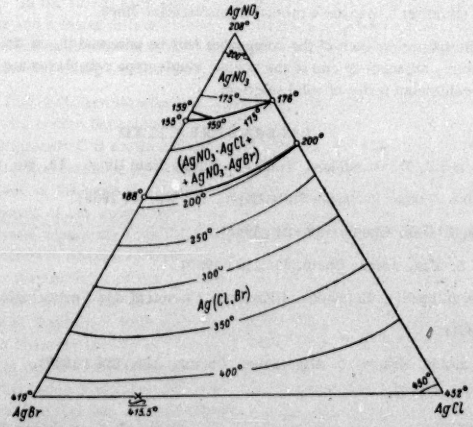

Fig. 6. Fusion diagram of the ternary system Ag‖Cl, Br, NO_3.

TABLE 2

Section No.	Starting Mixture	Melting point of Starting Mixture	Component added	Intersection Points of the crystallization branches		Crystallization Branches	Fig. No.
				%	Temp.		
1	93.5% $AgNO_3$ + 6.5% AgCl	201°	AgBr	18.5	158°	I and II	4
				41.5	189.5	II and III	
2	90% $AgNO_3$ + 10% AgCl	196	AgBr	14.5	160	I and II	4
				40.0	190	II and III	
3	90% $AgNO_3$ + 10% AgBr	192	AgCl	13.3	163	I and II	4
				28.0	198	II and III	
4	75% $AgNO_3$ + 25% AgCl	193	AgBr	21.5	194	II and III	4
5	75% AgBr + 25% AgCl	416	$AgNO_3$	55.0	194	III and II	5
				76.5	159	II and I	
6	50% AgBr + 50% AgCl	419	$AgNO_3$	58.5	194	III and II	5
				78.0	162	II and I	
7	60% $AgNO_3$ + 40% AgCl	250	AgBr	–	–	III	4
8	50% $AgNO_3$ + 50% AgCl	296	AgBr	–	–	III	4
9	74% $AgNO_3$ + 26% AgBr	160.5	AgCl	–	–	II	
10	70% $AgNO_3$ + 30% AgBr	171.0	AgCl	–	–	II	

Remarks. I) $AgNO_3$, II) solid solutions $AgNO_3 \cdot AgCl + AgNO_3 \cdot AgBr_3$, III) solid solutions Ag(Cl, Br).

SUMMARY

1. The ternary systems composed of potassium nitrate, chloride and bromide and of silver nitrate, chloride and bromide were studied by the visual-polythermal fusion method.

2. The liquidus surface for both of the systems consists of three crystallization fields: 1) continuous solid solutions of two components, 2) continuous solid solutions of compounds, melting with decomposition, and 3) third component. The extremes fail to have mutual crystallization lines.

3. Complete isomorphism for both of the compounds will be observed if, on the sides of the isotherm triangle of the ternary system, adjacent to one of the angles, single-type complexes are formed, and the corresponding components give a continuous series of solid solutions.

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THE RULE OF INVERSE SIMILITUDE

I. L. Krupatkin

Layer-formation in liquid mixtures is extensively used for the elucidation of the chemical activity taking place in them. To determine the reaction character between two components of a mixture it is studied by the method of layer-formation in the medium of a third component. In such a ternary system the chemical reactivity in one of its binary systems will predominate over those found in its other binary systems, and for this reason the indicated binary system in the given ternary is called the predominating system [1]. Chemical reactivity in the predominating system is expressed at the interlayer surface of the ternary system in the form of various-shaped geometric elements; here it should be kept in mind that the third component exerts an influence on the reactivity in the predominating system and participates in the formation of the variously shaped stratification regions found in the ternary system. Based on the character of the predominating system all ternary systems showing layer-formation can be divided into 5 series and each series into 3 groups, based on the increase in the number of stratified binary systems present in the given ternary system. On the basis of this a classification of the fundamental types of ternary systems with equilibrium between the liquid phases is shown in Fig. 1; in setting up this classification we used a procedure analogous to that used by M. A. Klochko [2] in deriving the types of electrical conductivity diagrams of binary systems. The following conditions were assumed in setting up the indicated classification: 1) the predominating system A-B is homogeneous; 2) under strong reactivity in the predominating system only one compound is formed in it; 3) the presented types of systems fail to combine between themselves; 4) in each type of system variations due to changes in the angles between the curves, or their mutual arrangement of curvature, are not examined. In the future each type of system will be designated by a group number, arranged in sequence, a series number and a letter differentiation, the latter emanating from the character of the geometric element on the stratification isotherm. A general rule can be found for all of these systems, the derivation of which and the conclusions that ensue from it being the purpose of the present study.

Of the systems in Fig. 1 the system isopropyl alcohol-isopropyl ether-water [3] serves as an example of type 2, 1, and for type 3, 1 the system benzoic acid-salicylic acid-water [4]. If through each of these systems the isoconcentrate mn of component C is drawn approximately through the middle of the stratification region, then it will divide the stratification isotherm into two parts, each of which is a qualitative reflection of the other, but of inverse curvature. Each of the parts of the isotherm fails to have any special or extreme points, which should also hold true in the absence of any compounds in the predominating system A-B, i.e. it reflects the character of the predominating system separately from the other part of the isotherm. The presence of a critical point on one of the isotherm branches in systems of type 2, 1 fails to alter what has been said above. Systems of type 1, 2 are realized in the other system forms of this series at elevated (or reduced) temperatures. The system pyridine-phenol-water [5] serves as an example of a type 2, 2 system, and the system phenol-water-phenylhydrazine [6] as an example of a type 3, 2 system. With respect to the predominating system A-B the isotherms of the ternary systems of this series are characterized by two minima. Each of the minima is found in the section, falling in the predominating system on the composition of the compound (or complex), and in that way establishes it. When the isotherms in this series of systems are cut by the isoconcentrate mn, the same as in the first series, then each minimum proves to be on its own separate branch. Consequently, both of the isotherm branches qualitatively resemble each other, but are of inverse curvature; each of them separately characterizes compound (or complex) formation in the system A-B. Systems of type 1, 3 can be realized at elevated temperatures in the remaining cases of this series. Type 2, 3, a is found in the system acetic acid-aniline-gasoline [7], while type 2, 3, b is found in the system phenyl mustard oil-aniline-sulfur [8]. The system acetic anhydride-water-gasoline [1] serves as an example of 3, 3, a type of system, while an example of the 3, 3, b type is the system allyl mustard oil-o-toluidine-sulfur [9]. Two singular points are found on the isotherms of these systesm; both of them are found on

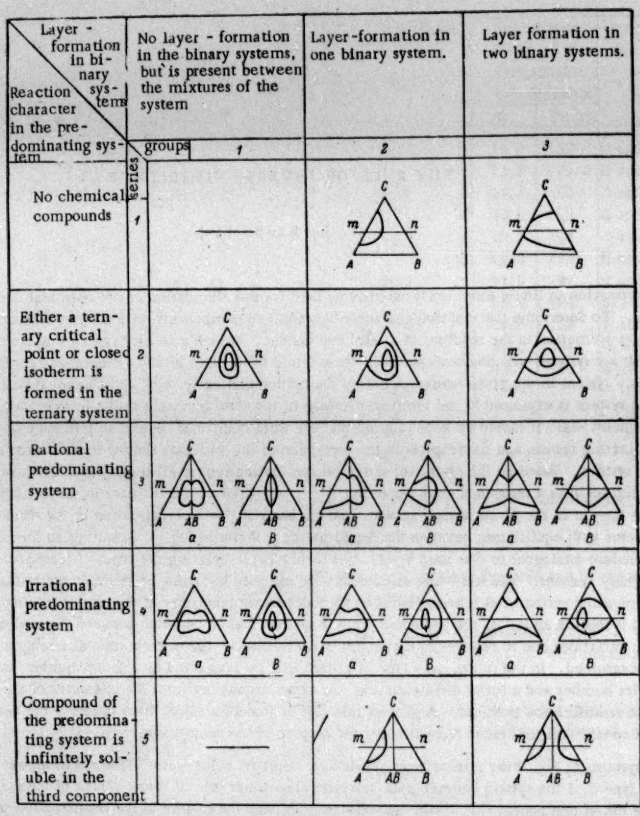

Fig. 1. Classification of ternary systems with layer-formation by the form of the isotherms.

the same quasibinary section C-AB of the ternary system, in the predominating system A-B corresponding to the composition of compound AB. If the isotherms of the systems in this series are divided by the straight line mn under the conditions of the previous cases, then their two branches are obtained, on each of which one singular point remains, each point separately fixing the same compound AB. Geometrically, the singular elements of the two branches are mirror images, but chemically they are the same. The 1, 4 type of system can originate in the remaining cases of this series under elevated (or reduced) temperatures. The 2, 4, a type of system can be formed in the systems of type 3, 4, a by elevating the temperature. The system piperidine-phenol-water [10] can serve as an example of the 2, 4, b type of system. For systems of type 3, 4, a the system diphenylamine-β-naphthylamine-sulfur [11] can serve as an example. The 3, 4, b type of system can be realized in the systems of type 2, 4, b by lowering (or raising) the temperature. In the systems of this series the isoconcentrate mn, drawn the same as in the previous cases, divides the isotherm into two qualitatively similar branches, each of which has an irrational extreme. Consequently, each branch separately characterizes the reactivity taking place in the predominating system. Geometrically the curvatures of the two branches are the opposite of each other. The system aniline-acetic acid-water [12] serves as an example of the 2, 5 type of system, while

the 3, 5 type is realized in the system water-ethyl alcohol-succinonitrile [13]. When compared with the systems of type 2, 1 the systems of this series, when their isotherms are cut by the isoconcentrates mn, fail to introduce anything new in the sense of the examined problem.

The presented material shows that one and the same rule is observed for all of the cases where there is equilibrium between the liquid phases in ternary systems, which rule can be named the inverse similitude rule and which can be formulated as follows: if in the concentration triangle of a ternary system with equilibrium between the liquid phases a straight line is drawn, parallel to the side of the binary predominating system and approximately through the middle of the plane, bounded by the solubility curves, then this isoconcentrate will divide the stratification isotherm into two branches, which branches will qualitatively resemble each other, but which will be the inverse of each other in curvature and in the arrangement of their geometric elements.

The inverse similitude rule, on the one hand, bears a qualitative character, since each of the branches of the stratification isotherm fails to be an exactly quantitative expression of each other. On the other hand, both branches have the same geometric elements, reflecting the appearance in the system of a qualitatively new compound, and in the absence of this compound, of qualitatively new (with respect to the condition of the component) association-dissociation processes for the molecules of the components in the mixtures. In this connection each branch separately reflects in a quantitative manner the character of the interactions taking place in the system, and the analogous geometric elements of both branches lie in the same section of the isotherm, proceeding from the angle of the third component to the side of the predominating system and in its composition corresponding to that of the compound or complex. On the strength of this the inverse similitude rule permits predicting the shape of the second branch of the stratification isotherm when one of them is present. This is important, first, in the case where the solubility of the components and mixtures of the predominating system in the third component is very small, i.e., when it is nearly impossible to study the second branch of the isotherm. In this case the described rule, by the appearance of one branch, permits judging as to the nature of the interactions taking place in the predominating system. Secondly, if it is necessary to make a preliminary study of the chemical activity taking place in the system the inverse similitude rule permits simplifying the study, limiting it to a study of one of the branches of the isotherm. In the first case it is necessary to study that branch of the isotherm that is adjacent to the side of the predominating system. In the second case it is necessary to study specifically the same branch, since it has the greater length, and all of the geometric elements stand out clearly on it. The isotherm branch located at the angle of the third component is very short, and small experimental errors or an insufficient number of studied mixtures can lead to omission or distortion of the geometric elements. The above-said is of fundamental importance for the reason that the branch of the stratification isotherms found in ternary systems that is adjacent to the side of the predominating system is to be considered as the main branch of the stratification isotherm of the ternary system.

The inverse similitude rule permits simplifying and relationalizing the classification of ternary systems showing layer-formation. If the classification shown in Fig. 1 was based on the appearance of the complete stratification isotherms, then in Fig. 2 the classification is depicted on the basis of the appearance of the main isotherm branches. In the latter figure each group of ternary systems is depicted separately in the form of rectangular diagrams, with an increase in the number of binary systems showing layer-formation in the given ternary the same as in Fig. 1. In each group the isotherms follow from top to bottom in the same series order as in Fig. 1. Counting off along the ordinate axis the percent of the liquid component C quantitatively expresses its solubility in the liquid mixtures of the predominating system, i.e., it expresses stratification as a property. The presented classification clearly shows the dependence of stratification and the character of its curves on the composition of the mixtures of the predominating system and on the interactions taking place in it. Together with this, such a classification converts the inconvenient representation of stratification curves on a triangular diagram into a generally accepted representation of the property curves of binary systems on a rectangular diagram. In this way the inverse similitude rule permits using stratification as a property when compared with the other properties of binary systems. A number of binary systems, studied by the method of stratification in a third component, can already be compared with their other properties. Thus, 16 properties are compared in the literature [14] for the system acetic anhydride-water, for which the acetic acid corresponds to a singular point on all curves. This binary system was also studied for layer-formation in gasoline [1] and carbon disulfide [15]; here the main isotherm branch was specifically studied, and in both cases the acetic acid again corresponds to a singular point.

The inverse similitude rule was derived for the individual stratification isotherms of ternary systems. Since it holds true for any isotherms, then its use is also valid for all of the polythermal prisms found in a ternary system. Fig. 3a shows this for the simple, but general case, where the stratification surface 5, 6, 7, 8, K_1 and K_2 of the

ternary system A-B-C connects the solubility breaks of its binary systems A-B and B-C. In the given case only, the sectioning line is replaced by the vertical plane 1, 2, 3 and 4, while the two parts of the stratification surface will resemble each other, being situated on the two sides of this plane. The inverse similitude rule is also applicable to binary and multicomponent systems. In Fig. 3b its application is shown to the general case of stratification in the binary system A-B with the formation in it of both upper and lower critical points K_1 and K_2, respectively. This system is analogous to the 1, 2 type of system, but here the critical points most frequently fail to lie on one vertical ; this same inverse similitude rule gives basis to the still insufficiently supported, but valid, opinion that the closed stratification polytherm is to be considered its general case in binary systems. This same assertion should also be extended to the closed stratification surfaces found in multicomponent systems. The application of the inverse similitude rule to quaternary systems is shown in Fig. 3c, here their simplest case of stratification in one binary system B-C was taken, made homogeneous in the tetrahedron of the quaternary system A-B-C-D. Here the plane A, 1, D, passing through the homogeneous system A-D and the stratified system B-C, divides the stratification surface 2, 3, 4, K of the quaternary system into two similar parts, found on the two sides of this plane.

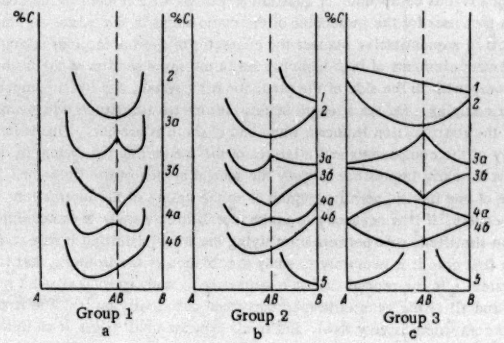

Fig. 2. Classification of ternary systems showing layer-formation by the form of the main isotherm branches. (See text.)

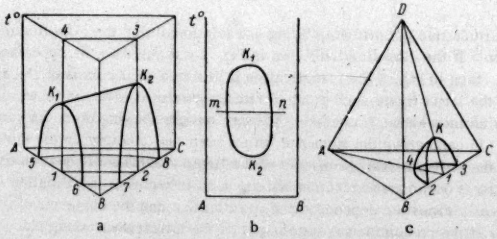

Fig. 3. Application of the inverse similitude rule to the polytherms of binary, ternary and quaternary systems. (See text.)

The inverse similitude rule permits making manifest the impossible cases of liquid-phase equilibria, and in that way it permits detecting faulty experiments. The simplest of these cases for binary and ternary systems are depicted in Figs. 4a and 4b, where the branches of the stratification curves, 1, K_1, 2 and 1, K_2, 2 in the first case, and 1, 2 and 3, 4 in the second case, although they resemble each other, are also the same in curvature, which is impossible. Nevertheless the case, presented in Fig. 4b, is encountered in the literature [16] in the qualitative representation of ternary systems, which is not correct.

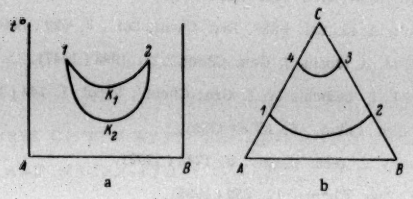

Fig. 4. Impossible cases of equilibrium between liquid phases. (See text.)

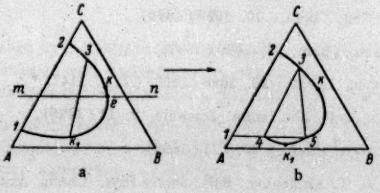

Fig. 5. Scheme for the rise of equilibrium for three liquid phases in ternary systems. (See text.)

The inverse similitude rule has definite limits: it is applicable to a two-phase liquid equilibrium and is not applicable to the equilibrium of three liquid phases. A scheme for the creation of such an equilibrium [17] is depicted in Fig. 5, in which connection 5a corresponds to the initial stage of the process at higher temperatures, where only one solubility minimum K_1 and critical conode 3, K_1 appears in the stratification region, while Fig. 5b corresponds to lower temperatures, where the already developed region of the three-phase liquid equilibrium 3, 4, 5 is present. As is shown in Fig. 5a, the straight line mn divides the stratification isotherm 1, K, 2 into two branches that fail to resemble eachother. Branch 2, e does not have any terminal points, while branch 1, e has a minimum K_1. As a result, the inverse similitude rule is not valid here, but this very fact has its positive side. Actually, the absence of a qualitative resemblance between the branches of the stratification isotherm in the system indicates that it is possible for the equilibrium of three liquid phases to arise in it.

SUMMARY

1. A rule was found for systems with equilibrium of two liquid phases, postulated as being a rule of inverse similitude, and applicable to binary, ternary and multicomponent systems.

2. The classification of ternary systems showing layer-formation was examined, and here it was shown that the proposed rule permits its simplification and rationalization. In this way conditions are created for comparing the stratification curves with the curves of other properties.

3. It was shown that the proposed rule permits predicting the form of one branch of the stratification isotherm provided the second branch of the isotherm is present, and in cases of necessity it permits judging as to the nature of the interactions taking place in the predominating system from the form of one branch. The rule creates conditions for the accelerated study of systems by the method of layer-formation.

4. It was shown that the described rule permits making manifest the impossible cases of liquid-phase equilibria, being a means for the detection of faulty experiments.

5. It was shown that the proposed rule is not applicable to systems with equilibrium of three liquid phases, but that this very fact is an indication that it is possible for a three-phase-liquid equilibrium to arise in the system.

6. The indicated rule gives basis to consider the two-phase liquid equilibrium with two critical points as being the general case in binary systems and indicates the necessity of considering the closed stratification surface as being the general case in multicomponent system.

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VAPOR PRESSURES OF THE SYSTEMS: WATER-ETHYL ALCOHOL-BENZOPHENONE AND WATER-ETHYL ALCOHOL-TRIPHENYLCARBINOL

M. I. Usanovich, V. F. Sergeeva and K. K. Khairulina

In 1891 it was established by I. Kablukov [1] that if sodium chloride is added to a mixture of water and ethyl alcohol that, when compared with the binary system alcohol-water, the total vapor pressure of the system is raised, as is also the partial pressure of the alcohol, while the partial vapor pressure of the water is lowered.

The total vapor pressure of the system water-methanol is increased when salts are dissolved in it, which increase becomes greater the higher the salt concentration and the more alkaline the salt [2]. Analogous data also exist with respect to the system water-ethyl alcohol-salt [3-7].

Up to now all of the vapor pressure studies have been made under the conditions of adding to the water-alcohol mixtures such substances as are readily soluble in water and show slight solubility in the alcohol, which situation led to a uniform influence on the nature of the vapor pressure curves.

Our problem was to study the influence of substances, soluble in alcohol and at the same time insoluble in water, on the vapor pressure of water-alcohol solutions.

In this paper we studied the vapor pressures of the following systems: water-ethyl alcohol-benzophenone and water-ethyl alcohol-triphenylcarbinol.

EXPERIMENTAL

The benzophenone and triphenylcarbinol were used after they had been recrystallized from alcohol and had m.p. 48.5° and 162.5°, respectively. The ethyl alcohol was dehydrated over calcium oxide and was distilled from metallic sodium. The fraction with b.p. 76° at 698 mm was collected.

Several milliliters of solution were distilled off in each experiment; this failed to essentially change the composition of the boiling solution (600 ml).

System Ethyl Alcohol-Water-Benzophenone. The change in the total and partial vapor pressures of the ternary system ethyl alcohol-water-benzophenone as a function of change in the composition of the solvent, but with the benzophenone concentration kept constant at 0.1M, was determined at 20, 40, 55 and 75°. The measurement results are given in Table 1 and shown in Figs. 1-4. The dotted curves designate the vapor pressure of the binary system, and the solid curves the vapor pressure of the ternary system.

Literature data [8] were used to construct the curves showing the relationship between the vapor pressure of the binary system ethyl alcohol-water and the composition; the control experiments showed excellent agreement with these data.

The measurement results showing the relationship between the total and partial vapor pressures of a water-alcohol mixture of constant composition (88% alcohol) and the benzophenone concentration are given in Table 2.

With increase in benzophenone concentration there is a decrease in the total vapor pressure at 20 and 40°, while at 55 and 75° there is an increase. The partial vapor pressure of the alcohol decreases, and that of the water increases (with some fluctuations at low benzophenone concentrations).

System Ethyl Alcohol-Water-Triphenylcarbinol. Due to the low solubility of the triphenylcarbinol the

change in the total and partial vapor pressures as a function of the triphenylcarbinol concentration was studied only for 90% alcohol. The results that were obtained are given in Table 3.

TABLE 1

Amount of alcohol (in wt. %)	P_{total} (in mm)				$P_{alcohol}$ (in mm)				P_{water} (in mm)			
	20°	40°	55°	75°	20°	40°	55°	75°	20°	40°	50°	75°
88.0	40	129	271	653	31.0	104.5	218.0	487.0	9.0	24.5	53.0	166.0
69.9	36	117	251	614	22.5	75.0	157.0	366.5	13.5	42.0	94.0	247.5
48.4		105	230	567		58.0	126.5	308.5		47.0	103.5	258.5

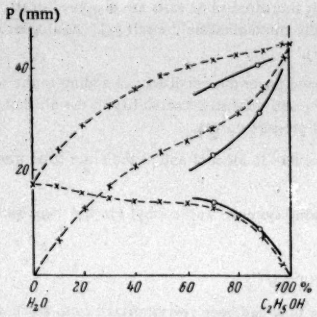

Fig. 1. Change in the vapor pressure of the system ethyl alcohol-water-benzophenone at 20° as a function of the solvent composition.

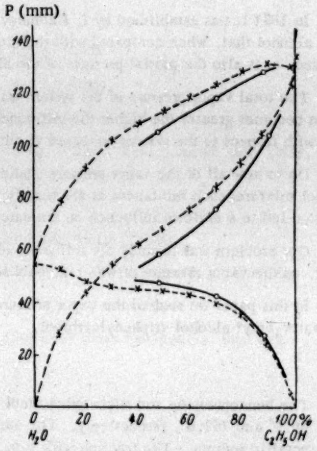

Fig. 2. Change in the vapor pressure of the system ethyl alcohol-water-benzophenone at 40° as a function of the solvent composition.

TABLE 2

Benzophenone concentration (in mole/liter)	P_{total} (in mm)				$P_{alcohol}$ (in mm)				P_{water} (in mm)			
	20°	40°	55°	75°	20°	40°	55°	75°	20°	40°	55°	75°
0	42	131	272	655	33	103.5	216	515	9	27.5	56	140
0.1	40	129	271	654	31	104	216	488	9	25	55	166
0.2	39	125	279	658	30	99	215	486	9	26	64	172
0.4	39	123	280	658	30	92	209	477	9	31	71	181

The data given in Table 3 show that at 55 and 75° the total vapor pressure increases slightly, the partial vapor pressure of the alcohol decreases, and that of the water increases with increase in the triphenylcarbinol concentration. The effects of changing the vapor pressures as a function of change in the triphenylcarbinol concentration are not exact because of the small concentrations of dissolved substance, since triphenylcarbinol is poorly soluble even in 90% alcohol.

TABLE 3

Triphenylcarbinol concentration (in mole/liter)	P_{total} (in mm)			$P_{alcohol}$ (in mm)			P_{water} (in mm)		
	40°	55°	75°	40°	55°	75°	40°	55°	75°
0	129	272	656	104.5	224	526.0	24.5	48	130.0
0.05	129	272	655	104.0	220	512.5	25.0	52	142.5
0.10	127	271	655	103.0	217	507.0	24.0	54	148.0
0.15	127	276	661	102.0	208	505.5	25.0	68	155.5

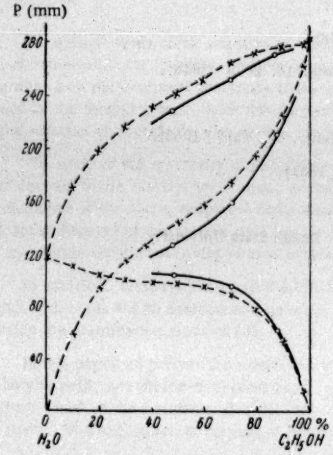

Fig. 3. Change in the vapor pressure of the system ethyl alcohol-water-benzophenone at 55° as a function of the solvent composition.

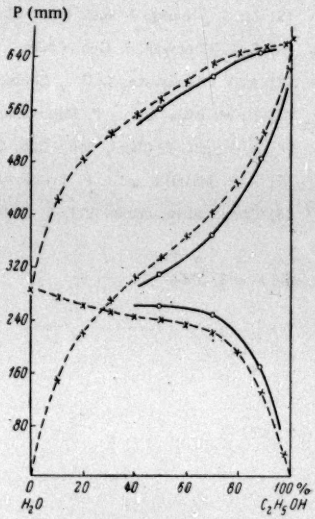

Fig. 4. Change in the vapor pressure of the system ethyl alcohol-water-benzophenone at 75° as a function of the solvent composition.

DISCUSSION OF RESULTS

We studied the changes in the vapor pressures of water-alcohol solutions when substances, soluble only in the alcohol and insoluble in water, were added. The dissolving of benzophenone and triphenylcarbinol in mixtures of water and alcohol causes a lowering of the alcohol partial vapor pressure and an increase in the water partial vapor pressure. As a result, the added substance causes a lowering in the partial vapor pressure of that component of the solvent mixture in which it dissolves. The physicochemical equilibrium of the given system is upset if a third substance is added to the mixed solvent. The substances, soluble only in the alcohol, bind the alcohol molecules and correspondingly free the water, as a result of which the partial vapor pressure of the alcohol is lowered and the partial vapor pressure of the water is raised. Consequently, by measuring the partial vapor pressures of three-component systems and comparing them with the vapor pressure of the binary system, it becomes possible to judge the nature of the interactions that take place in solution.

SUMMARY

1. The change in the vapor pressure of the system benzophenone-water-ethyl alcohol as a function of

the solvent composition was studied at 20, 40, 55 and 75°. When compared with the binary system alcohol-water, in this system the total vapor pressure is lowered, the partial vapor pressure of the alcohol is also lowered and the partial vapor pressure of the water is raised.

2. The change in the vapor pressure as a function of change in either the benzophenone or triphenylcarbinol concentration, with the solvent composition kept constant, was also studied (at the above-indicated temperatures). The partial vapor pressure of the alcohol is lowered and that of the water is raised with increase in the concentration of either the benzophenone or the triphenylcarbinol.

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STUDY OF THE REACTION OF ACETAMIDE WITH SOME ALIPHATIC ACIDS BY PHYSICO-CHEMICAL ANALYSIS METHODS

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Our earlier study of the reaction of urea with carboxylic acids [1, 2] permitted us to establish the formation of complexes, the stability of which depends on the nature of the acid component. It was of interest to determine how the chemical reactivity character would be affected if one of the amino groups in urea was replaced by the methyl group. With this purpose in mind we undertook a study of a number of systems, formed by the reaction of acetamide with various carboxylic acids.

The study of the reactivity of acetamide with various acids is an intermediate one in a series of investigations devoted to the reactivities of urea, acetamide and acetone with the same acids. By comparing the reactivity character of the above-indicated components it may be possible to answer in some measure the question, still being disputed at the present time, as to which of the atoms – the electron donors (oxygen or nitrogen) – are responsible for the reactivity of urea with acids.

In addition, these studies pursued a different goal: to elucidate the possibility of forming acetamide compounds with acids and to determine their relative stability in the liquid phase, which is of importance for understanding the reamination reaction [3].

In this paper we present the results of studying the four binary systems: acetamide-acetic acid, acetamide--n-butyric acid, acetamide-n-caproic acid, and acetamide-stearic acid. The physico-chemical analysis methods based on the fusibility, density, viscosity and electrical conductivity of the system were used in making the study. The experimental method of operation was described by us earlier [4].

The concentrations were expressed in mole percents, the viscosities in centipoises.

The commercially pure grade of acetamide was purified by being distilled 3 times. The fraction with b.p. 121.2° was used. The acetamide had m.p. 79.4°, d_4^{80} 0.9990, η_{80} 1.61, centipoises, κ_{80} $36.2 \cdot 10^{-6}$ $\Omega^{-1} \cdot cm^{-1}$.

The System Acetamide-Acetic Acid was studied earlier by the fusion method [5, 6] and the presence of a compound, melting with decomposition and having a 1:1 composition, was established. The fusion curve, based on the data of N. A. Albansky [6], is shown in Fig. 1. We studied this system in the liquid phase by the fusion, viscosity and electrical conductivity methods at temperatures of 70, 80 and 90°.

The acetic acid used in our work was purified as before [7], and had m.p. 16.6°.

The isotherms, expressing the relationship between the density in the system and the composition, are shown in Fig. 2. The curves are slightly convex to the composition axis.

The viscosity isotherms (Fig. 2) are S-shaped curves with an inflection point, appearing at approximately 60 mole % of acetamide. A well defined maximum is found on the electrical conductivity isotherms (Fig. 1), appearing at approximately 50 mole % of acetamide. The maximum shifts toward the acetic acid side as the temperature is raised. The temperature coefficient of the electrical conductivity has its maximum value in this region. Correction of the electrical conductivity for viscosity (mm) fails to change the character of the curves.

System Acetamide-n-Butyric Acid. The butyric acid taken for the work, after purification [1], had b.p. 197.6°.

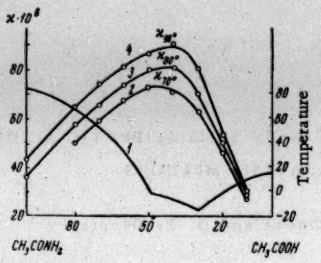

Fig. 1. Fusibility (1) and electrical conductivity (2-4) of the system acetamide-acetic acid.

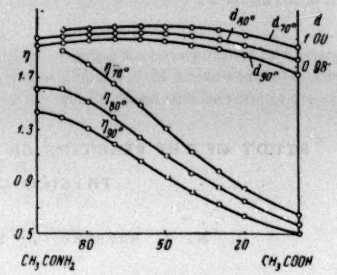

Fig. 2. Density and viscosity of the system acetamide-acetic acid.

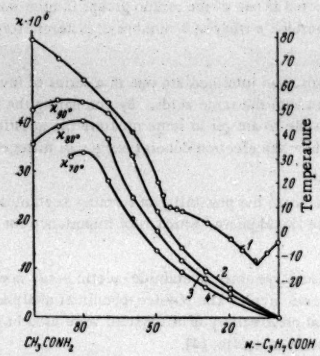

Fig. 3. Fusibility (1) and electrical conductivity (2-4) of the system acetamide-butyric acid.

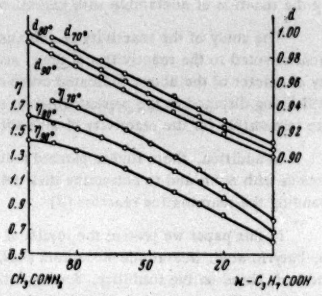

Fig. 4. Density and viscosity of the system acetamide-butyric acid.

The fusion curve of the system (Fig. 3) consists of three branches – two crystallization branches of the pure components and one crystallization branch of a compound of probable composition $CH_3CONH_2 \cdot C_3H_7COOH$, melting with decomposition. At the eutectic point with m. p. −12.7° the mixture contains 9 mole % of acetamide, and at the transition point with m. p. 10°−47 mole % of acetamide.

The density isotherms of the system (Fig. 4) appear as nearly straight lines.

The viscosity isotherms (Fig. 4) are slightly convex to the composition axis, in which connection the curvature of the lines becomes somewhat smoother with temperature elevation.

The electrical conductivity increases slightly when small amounts of butyric acid are added, and then beginning with 70 mole % of acetamide (Fig. 3) it drops sharply.

System Acetamide-n-Caproic Acid. After two distillations through a dephlegmator the C. P. caproic acid had m. p. 201.6°; m. p. −1.5°.

The fusion diagram of the system is shown in Fig. 5. The fusion curve very closely resembles the comparable curve of the preceding system. The middle branch corresponds to the crystallization of a compound that melts with decompostion and in all probability has the composition $CH_3CONH_2 \cdot C_5H_{11}COOH$. The eutectic point with m. p. −12° corresponds to 13 mole % of acetamide, and the transition point with m. p. 7.5° to 48 mole % of acetomide.

The density isotherms (Fig. 6) appear convex to the composition axis. The viscosity isotherms (Fig. 6) pass through a maximum in the region of 60 mole % of acetamide. The temperature coefficient of the viscosity has its maximum value in the same region. With elevation of the temperature, as in the preceding system, the curves straighten out. The electrical conductivity isotherms (Fig. 5) have an S-shaped form. In contrast to the preceding system, the electrical conductivity of acetamide drops when even very small amounts of caproic acid are added.

System Acetamide-Stearic Acid. After 3 recrystallizations from benzene the stearic acid had m. p. 68.8°.

The fusion diagram of the system is shown in Fig. 7, and consists of two crystallization branches of the pure components, intersecting in the eutectic point, which corresponds to 48 mole % of acetamide (m. p. 58.7°). Strong supercooling is observed in the region from 60 to 20 mole % of acetamide, which we were unable to eliminate, either by vigorous stirring or with a seed crystal. The temperatures shown in the figure are the averages of 7-10 determinations.

The density isotherms (Fig. 8) drop sharply in the region from 100 to 70 mole % of acetamide, and then descend smoothly. The viscosity of the system (Fig. 8) rises strongly at first, passing through a maximum in the region of 70 mole % of acetamide and then descends gently. The electrical conductivity of the system is determined by the comparatively greater conductivity of acetamide. The addition of the practically nonconducting stearic acid results in a sharp decrease in the electrical conductivity, which at 20 mole% of acetamide becomes less than $1 \cdot 10^{-10}$ $\Omega^{-1} \cdot cm^{-1}$.

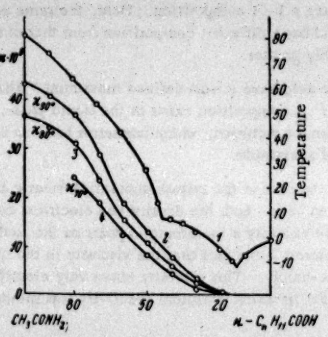

Fig. 5. Fusibility (1) and electrical conductivity (2-4) of the system acetamide-n-caproic acid.

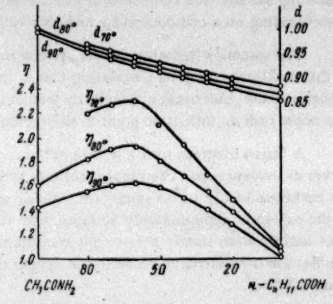

Fig. 6. Density and viscosity of the system acetamide-n-caproic acid.

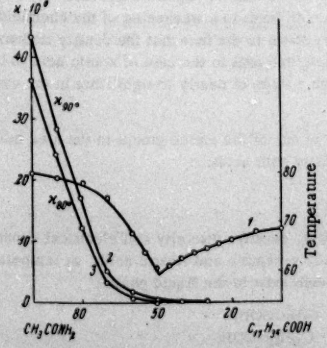

Fig. 7. Fusibility (1) and electrical conductivity (2, 3) of the system acetamide-stearic acid.

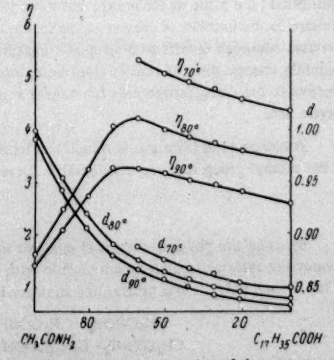

Fig. 8. Density and viscosity of the system acetamide-stearic acid.

We were unable to study the systems of acetamide with the mono-, di- and trichloroacetic acids in the liquid phase for the reason that the mixture decomposed at temperatures above 50-70° over nearly the whole concentration range.

DISCUSSION OF RESULTS

A study of the system acetamide-acetic acid showed that the compound $CH_3CONH_2 \cdot CH_3COOH$, established by the fusibility method, also exists in the liquid phase. Chemical reactivity here finds expression in the density, viscosity and electrical conductivity curves. The inflection point on the S-shaped viscosity curves appears at approximately 50 mole % of acetamide, and the maximum of the electrical conductivity isotherms also appears in the same region. The position of these points indicates that the compound $CH_3CONH_2 \cdot CH_3COOH$ is also capable of existing in the liquid phase. When a comparison is made of the character of the chemical reactivity of urea and acetamide with acetic acid it can be seen that acetamide with acetic acid gives a compound of different composition than does urea [1], and that the stability of the acetamide compound with acetic acid is much greater than the stability of the corresponding urea compound.

The fusion diagram of the system acetamide-butyric acid reflects the formation of a compound, melting with decomposition and having the probable composition $CH_3CONH_2 \cdot C_3H_7COOH$. The positive deviation of the viscosity isotherms in the system acetamide-butyric acid from strict (linear) additivity is evidence that in the liquid phase also there is chemical reactivity between the components. Of interest is the form of the electrical conductivity curves, possessing an S-shaped character. Such curves are known for systems showing chemical reactivity [8, 9]. It is difficult to judge the composition of the compound in the liquid phase from the form of the viscosity isotherms. The electrical conductivity isotherms, having an inflection point in the region of 50 mole % of acetamide, give some indication that the compound may have a 1 : 1 composition. Here, the same as in the preceding system, the compound of acetamide with butyric acid has a different composition from that of the corresponding urea compound [1], and its stability is considerably greater.

The viscosity isotherms for the system acetamide-caproic acid have a well defined maximum. The position of this maximum permits postulating that a compound with a 1 : 1 composition exists in the liquid phase. An analysis of the electrical conductivity isotherms leads to the same conclusion, which isotherms have an S-shaped character with an inflection point in the region of 50 mole % of acetamide.

A fusion diagram with a simple eutectic was obtained in the case of the system acetamide-stearic acid, which serves as evidence that chemical reactivity is absent in the given case. Both the density and electrical conductivity isotherms testify to the same fact. However, in studying the viscosity a maximum appears on the isotherms in the region of approximately 50 mole % of acetamide. Of interest is the fact that the viscosity in the system rises slightly from stearic acid to the maximum, and then drops sharply. This viscosity curve very closely resembles the corresponding curve in the system urea-resorcinol [9], in which chemical reactivity was shown by other methods.

On comparing the property curves of the four systems studied by us it can be concluded that with increase in the length of the acid chain the chemical reactivity between the components in the systems not only fails to be diminished (the same as for urea), but even increases somewhat in the case of caproic acid, and only a large increase in the number of carbon atoms in the radical (stearic acid) leads to a weakening of the chemical reactivity, although it fails to destroy it completely. Attention is drawn to the fact that the density isotherms gradually change their character from being convex to the composition axis in the case of acetic acid to being concave to the composition axis for stearic acid, passing through a stage of nearly straight lines in the case of butyric acid.

It can be seen from the obtained results that replacement of one of the amino groups in the urea molecule by the methyl group leads to considerable increase in the reactivity with acids.

SUMMARY

By using the physico-chemical analysis methods of fusibility, density, viscosity and electrical conductivity to study the systems formed by acetamide with acetic, n-butyric, n-caproic and stearic acids, at temperatures of 70, 80 and 90°, it was established that the following compounds exist in the liquid phase :

$CH_3CONH_2 \cdot CH_3COOH$, $CH_3CONH_2 \cdot C_3H_7COOH$,
$CH_3CONH_2 \cdot C_5H_{11}COOH$ and $CH_3CONH_2 \cdot C_{17}H_{35}COOH$.

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* T. p. = C. B. Translation pagination

THE REACTION OF COBALT HALIDES WITH ANABASINE

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In a previous paper it was shown by one of us [1] that cobalt chloride in hydrochloric acid medium forms two compounds with anabasine, namely $COCl_2 \cdot C_{10}H_{14}N_2 \cdot HCl$ and $COCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl$. The first compound is obtained by introducing the calculated amount of hydrochloric acid into the reaction, while the second compound is formed when an excess of hydrochloric acid is present. The composition of the second compound fails to be changed even if the synthesis is run in a large excess of hydrochloric acid. Salts of analogous composition were also obtained with the chlorides of zinc [2], cadmium [3], mercury [4] and copper [5]. The composition and properties of these salts permit assuming that they are all salts of anabasine and the corresponding chloro acids of composition $HMeCl_3$ and H_2MeCl_4, where Me is the metal.

In this paper we give the results obtained in studying the reaction of anabasine with cobalt bromide and cobalt iodide, respectively run in hydrobromic acid and hydriodic acid medium.

EXPERIMENTAL

All of the compounds described below were prepared by the same general method: first the cobalt bromide and cobalt iodide acid complexes were prepared by treating the calculated amount of cobalt carbonate with the exactly calculated amounts of hydrobromic or hydriodic acid, then to the obtained solution under vigorous stirring was added dropwise the predetermined amount of anabasine. The solution was evaporated on the water bath to incipient crystallization.

We used the Ilyin method [6] of reducing bromine with sulfur dioxide to prepare the hydrobromic acid. The hydriodic acid was purified by distillation from red phosphorus, in which connection the fraction distilling at 126° was used for reaction.

$CoBr_2 \cdot C_{10}H_{14}N_2 \cdot HBr$. Cobalt carbonate (4.2 g) was dissolved in 10 g of 45% hydrobromic acid. The solution was filtered and to the filtrate was added 3 g of anabasine. Evaporation of the solution on the water bath gave a dark-blue crystalline substance. This substance was recrystallized twice from water, dried at 100-105° to constant weight, and then analyzed for its content of cobalt, nitrogen and halogen. The cobalt was determined gravimetrically as $CoNH_4PO_4 \cdot H_2O$ [7] and also potentiometrically [8]. For the second method a sample of the substance weighing about 0.1-0.3 g was dissolved in 10 ml of water. To the resulting solution was added 10 ml of 15% ammonia and 1 g of dry ammonium chloride. When the ammonium chloride had dissolved, the divalent cobalt was oxidized to the trivalent state with an excess of standard potassium ferricyanide solution. The excess of the latter was then determined potentiometrically, using a platinum electrode and standard cobalt chloride solution. The nitrogen was determined by the Dumas micromethod, and the halogen by both gravimetric and potentiometric methods.

Found %: Co 12.78 (gravimetrically), 12.82, 12.71 (potentiometrically); N 5.92, 5.96; Br 51.90, 51.89. $CoBr_2 \cdot C_{10}H_{14}N_2 \cdot HBr$. Calculated %: Co 12.77; N 6.06; Br 51.90.

The substance melts at 312° with decomposition.

$CoBr \cdot C_{10}H_{14}N_2 \cdot 2HBr$. Cobalt carbonate (5.4 g) was dissolved in 18 g of 45% hydrobromic acid, and excess of which fails to exert an influence on the composition of the compound that is formed. To the filtered solution was added 4 g of anabasine, and the solution was evaporated on the water bath. The azure blue crystals obtained here were recrystallized twice from water and then dried to constant weight at 100-105°. The obtained salt melts at 290° (with decomp.).

Found %: Co 10.80, 10.93, 10.88; N 4.96, 4.99; Br 59.16, 59.00.
$CoBr_2 \cdot C_{10}H_{14}N_2 \cdot 2HBr$. Calculated %: Co 10.90; N 5.16; Br 59.10.

$CoI_2 \cdot C_{10}H_{14}N_2 \cdot HI$. Cobalt carbonate (4.2 g) was dissolved in 12.6 g of 57% hydriodic acid. To the solution, after it had been filtered, was added 3 g of anabasine and the solution was evaporated on the water bath. A green-colored crystalline substance was obtained. The compound was well-washed with ether and then dried. M.p. 270° (with decomp.).

Found %: Co 10.23, 10.34; N 4.58, 4.67; I 63.14, 63.13. $CoI_2 \cdot C_{10}H_{14}N_2 \cdot HI$. Calculated %: Co 10.23, N 4.64; I 63.15.

$CoI_2 \cdot C_{10}H_{14}N_2 \cdot 2HI$. Cobalt carbonate (8.4 g) was dissolved in 18 g of 57% hydriodic acid. As in the previous case, an excess of acid fails to be harmful. To the filtered solution was added 6 g of anabasine. Evaporation of the solution on the water bath gave yellow-green crystals. The crystals were repeatedly washed with ether and then dried. The obtained compound melts at 250° (with decomp.).

Found %: Co 8.23, 8.21; N 3.75, 3.81; I 69.09 69.21. $CoI_2 \cdot C_{10}H_{14}N_2 \cdot 2HI$. Calculated %: Co 8.06; N 3.84; I 69.47.

The somewhat low analysis results obtained for the iodine content is explained, apparently, by the tendency of the obtained compound to be oxidized in the air with the liberation of free iodine.

When the melting points of the salts obtained by us are compared with the melting points of the compounds

$$CoCl_2 \cdot C_{10}H_{14}N_2 \cdot HCl \text{ and } COCl_2 \cdot C_{10}H_{14}N_2 \cdot 2HCl,$$

and also with the corresponding zinc, cadmium and copper compounds, the following can be noted: 1) among the cobalt salts the bromide salts have the highest melting point; the cobalt, zinc and cadmium salts, into whose composition 1 mole of acid enters, possess a higher melting point than do the corresponding compounds with 2 moles of acid. The reverse relationship is observed for the copper salts.

All of the salts obtained by us are soluble in water. The colors of the aqueous solutions are: $CoBr_2 \cdot C_{10}H_{14}N_2 \cdot HBr$ – pinkish-yellow, $CoBr_2 \cdot C_{10}H_{14}N_2 \cdot 2HBr$ – pink, $CoI_2 \cdot C_{10}H_{14}N_2 \cdot HI$ – pink, and $CoI_2 \cdot C_{10}H_{14}N_2 \cdot 2HI$ – yellow. The solubility of the obtained salts in water is noticeably increased in the presence of ammonium chloride.

Hydrogen sulfide water easily precipitates the black cobalt sulfide from aqueous solutions of these salts, while silver nitrate precipitates all of the halogen ions. Consequently, free cobalt and halogen ions are present in the aqueous solutions. From this it follows that all of the compounds obtained by us are salts of the corresponding cobalt hydrobromides and hydriodides.

SUMMARY

1. The complexes of anabasine with cobalt iodide and bromide and the corresponding acids were obtained, which complexes have the composition:

$CoBr_2 \cdot C_{10}H_{14}N_2 \cdot HBr$, $CoBr_2 \cdot C_{10}H_{14}N_2 \cdot 2HBr$.
$CoI_2 \cdot C_{10}H_{14}N_2 \cdot HI$, $CoI_2 \cdot C_{10}H_{14}N_2 \cdot 2HI$.

2. For the cobalt, zinc and cadmium salts it was noted that the compounds of anabasine with the complex acids of the type $C_{10}H_{14}N_2 \cdot HMeX_3$ have higher melting points than do the compounds of the type $C_{10}H_{14}N_2 \cdot H_2MeX_4$ (where X = halogen).

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THE CLEAVAGE OF TRIPHENYLANTIMONY WITH HALO DERIVATIVES OF HYDROCARBONS IN THE PRESENCE OF ALUMINUM CHLORIDE

M. S. Malinovsky and S. P. Olifirenko

In a previous paper [1] we communicated that the action of acid chlorides on triphenylantimony in the presence of aluminum chloride leads to the formation of aliphatic aromatic ketones, which ketones are formed as the result of the cleavage of phenyl radicals from the stibine. However it seemed possible to us to split off the phenyl radicals from antimony, not only with acid chlorides, but also with the halo derivatives of hydrocarbons, which is the subject of the present communication.

As is known, in the synthesis of ketones and keto acids by the Friedel-Crafts reaction the reagents in the limiting case are taken in molar quantities, whereas for the monoalkylation of the aromatic hydrocarbons it is necessary to have a greater amount of the hydrocarbon present than of the alkylating agent and catalyst. These same rules were also observed by us in the papers that we examined. When the $R-C\overset{O}{\diagup}$ group is introduced, either into triphenylantimony or into an aromatic haloarsine [2], it is necessary to take one part of the acid chloride and one part of aluminum chloride for each phenyl radical. Only in such manner is it possible to achieve complete cleavage of the C_6H_5- from the stibine or arsine.

It was experimentally shown that analogous results are obtained in the alkylation of triphenylantimony if for each pheny radical of triphenylantimony 1.0 mole of alkyl halide is taken, while the aluminum chloride can be taken in an amount of either 1.0 mole or 1/3 mole. Considerable amounts of the aluminum chloride remain unchanged if it used in large excess.

The halo derivatives taken by us were ethyl, isopropyl, butyl, isobutyl and isoamyl bromides; in addition, benzyl chloride, bromobenzene and chloroform. Of these the first five with triphenylantimony form the corresponding alkylbenzenes (in yields ranging from 35 to 58%), the formation of which can be expressed by the following equation:

$$(C_6H_5)_3Sb + 3BrR \rightarrow 3C_6H_5 - R + SbBr_3.$$

In addition to the alkylbenzenes the reaction products were found to contain antimony bromide (determined as antimony sulfide) and some tar, the latter containing a small amount of antimony. However, in the case of ethyl bromide the formation of a small amount of $(C_6H_5)_2(C_2H_5)SbBr_2$ was also observed. With none of the other alkyl halides were analogous compounds obtained.

With benzyl chloride only a 19% yield of diphenylmethane was obtained. In this case some unchanged triphenylantimony was also isolated, which situation failed to be observed for the above examined alkyl halides. On the basis of the amount of antimony sulfide that was precipitated by hydrogen sulfide from the reaction products after their treatment with water it can be concluded that 77.7% of the antimony was always split off as antimony trichloride when the taken triphenylantimony was exposed to the action of benzyl chloride.

With bromobenzene 52.7% of the triphenylantimony taken for reaction was recovered unchanged. In addition to the latter, there was also obtained a small amount of diphenyl, diphenylantimony bromide and antimony tribromide (the latter as antimony sulfide).

We failed to obtain the expected triphenylmethane when triphenylantimony was cleaved with chloroform

TABLE

Substances Obtained in the Cleavage of Triphenylantimony

Exp. No.	Halide derivatives	Hydrocarbon of type C_6H_5-R is formed	Boiling point	d_4^{20}	n_D^{20}	Yield $(C_6H_5)_3Sb$ (in %)	Other substances and residue	Melting point	Obtained (in g)	Found antimony (in %)	Precipitated Sb_2S_3 (in g)
1	C_2H_5Br	$C_6H_5C_2H_5$ [5]	136°	0.8678	1.4962	35.2	$(C_6H_5)_2(C_2H_5)SbBr_2$	158°	4.9	26.15	6.5
							Residue	–	3.3	2.03	–
2	iso-C_3H_7Br	$C_6H_5CH(CH_3)_2$	152	0.8628	1.4927	48.8	Residue	–	8.2	11.23	7.2
3	n-C_4H_9Br	$C_6H_5C_4H_9$	183	0.8658	1.4931	57.6	Residue	–	3.2	14.28	7.8
4	iso-C_4H_9Br	$C_6H_5C_4H_9$-iso	170-171	0.8679	1.4965	43.3	Residue	–	6.4	9.7	7.5
5	iso-$C_5H_{11}Br$	$C_6H_5C_5H_{11}$-iso	197-199	0.8608	1.4859	34.2	Residue	–	6.8	8.5	7.6
6	$C_6H_5CH_2Cl$	$(C_6H_5)_2CH_2$	m. p. 26	–	–	19.4	$(C_6H_5)_3Sb$	51-52	2.6	34.27	6.6
							Residue	–	17.0	2.6	
7	C_6H_5Br						$(C_6H_5)_3Sb$	51-52	9.3	34.48	0.5
							$(C_6H_5)_2$	70	0.7	–	
8	$CHCl_3$						$(C_6H_5)_2SbBr$		3.8	34.0	–
							Residue	–	12.0	1.7	–
							$(C_6H_5)_3Sb$	51-52	0.3	34.3	2.2
							$(C_6H_5)_2$	69-70	0.3	–	
							Residue	–	4.5	19.2	–

in carbon disulfide medium in the presence of aluminum chloride. Unchanged triphenylantimony, a small amount of diphenyl and antimony chloride (isolated as antimony sulfide) were found in the reaction products. The results of this experiment differ somewhat from the data obtained by Z. A. Manulkin and A. N. Tatarenko [3], who ran the cleavage of the triphenylantimony in chloroform medium, and not in carbon disulfide.

In none of the experiments made by us were we able to detect the presence of benzene, the formation of which could have been expected.

EXPERIMENTAL

For each experiment we took 17.65 g (or 0.05 mole) of triphenylantimony, 3 moles of the halogenated hydrocarbon for 1 mole of triphenylantimony, and either 3.0 or 1.0 mole equivalents of aluminum chloride. We will describe the cleavage of triphenylantimony using n-butyl bromide; all of the other experiments are summarized in the table, in which connection, since our cleavage results using different amounts of aluminum chloride (for the same halogen derivative) differed but slightly among themselves, the experiment is described only once.

The triphenylantimony was obtained by the Michaelis method [4] and was purified by vacuum-distillation. It melted at 49-50°. The halide derivatives used were either of Kahlbaum quality (C.P.) or were obtained from the alcohols by the proper method.

For the cleavage of triphenylantimony with n-butyl bromide there was taken:

$(C_6H_5)_3Sb$ 17.65 g, n-C_4H_9Br 20.55 g and $AlCl_3$ 20.0 g

The triphenylantimony was dissolved in 100 g of carbon disulfide in a three-necked flask, fitted with stirrer, reflux condenser and dropping funnel. Anhydrous freshly distilled aluminum chloride was added to the flask when all of the triphenylantimony had dissolved, and then the n-butyl bromide was added dropwise over 1.5 hours with stirring and ice-cooling of the flask. The reaction mixture, separating into two layers, was allowed to stand overnight, and then was heated on the water bath until the evolution of hydrogen bromide had ceased. The subsequent operations were analogous to those described earlier [1, 2]. After removing the carbon disulfide the 16.2 g of residue was vacuum-distilled. The yield of distilled liquid was 12.6 g boiling in the range of 82-100° at 14 mm. The residue in the flask weighed 3.2 g. The liquid fraction was treated in the cold with concentrated sulfuric acid to remove any antimony compounds, after which it was distilled. There was obtained 11.6 g of butylbenzene with b.p. 183-184°, d_4^{20} 0.8658, n_D^{20} 1.4931, which correspond to the literature data for this substance [5]. The residue (tar) was found to contain 14.28% of antimony, while treatment of the water layer, formed after decomposing the reaction mixture with ice, with hydrogen sulfide gave 7.8 g of antimony sulfide, which was confirmed by determining its antimony and sulfur content.

SUMMARY

1. The cleavage of phenyl radicals from triphenylantimony is observed when the triphenylantimony is reacted with alkyl halides in the presence of aluminum chloride in carbon disulfide medium, which phenyl radicals form the corresponding alkyl hydrocarbons.

2. Triphenylantimony is cleaved to a slight degree by bromobenzene with the formation of diphenyl, diphenylantimony bromide and antimony bromide, the latter being determined as antimony sulfide.

3. Triphenylmethane fails to be formed when chloroform is reacted with triphenylantimony in carbon disulfide medium; here a small amount of diphenyl and antimony chloride is obtained.

4. In not one of our examined reactions could we establish the formation of benzene.

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CONTACT CONVERSION OF CYCLOOLEFINIC HYDROCARBONS WITH UNSATURATED SIDE CHAINS IN THE PRESENCE OF GUMBRIN

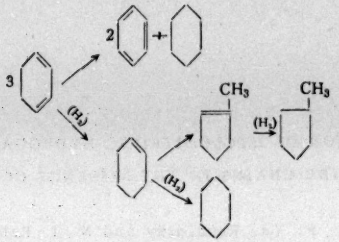
F. Yu. Rachinsky and N. I. Rzhekhina

The contact conversions of cycloolefins with unsaturated bonds in the side chain in the presence of the natural aluminosilicates have been studied but slightly up to now. Venable [1], in passing dipentene over floridine, found that the main isomerization product is α-terpinine. G. A. Rudakov [2], on heating dipentene with activated clay at 160-180°, found the polymerization products of pentene (~72%) and approximately equal quantities of 2-menthene and p-cymene in the catalyzate. This gives a basis for assuming that in isomerization of dipentene over clay and floridine the primary reaction is the shifting of the double bond from the side chain into the ring, while the redistribution of hydrogen is the secondary process. Ya. M. Slobodin [3], in studying the isomerization of 1-vinyl-3-cyclohexene and 1-limonene over floridine at 200-235°, established that only shifting of the double bonds and formation of a conjugated system takes place under the indicated conditions. In studying the contact conversion of 1-methyl-3-propenyl-5-cyclohexene over gumbrin it was shown by one of us [4] that here the isomerization and hydrogen redistribution processes proceed in accord with the scheme proposed by R. A. Levina [5]. The shifting of the double bonds from the side chain into the ring leads to the intermediate formation of cyclohexadiene hydrocarbons, which as the result of irreversible catalysis [6] forms a mixture of cycloaliphatic and aromatic hydrocarbons. There is also parallel formation of the polymeric forms. The ability of dipentene to undergo irreversible catalysis in presence of certain oxides was also confirmed in later studies [7].

Since the mechanism for the contact conversion of cycloolefins with unsaturated bonds in the side chain over natural aluminosilicates is treated differently by different investigators, we decided to undertake the study of the contact conversion over gumbrin of a number of cyclic hydrocarbons, containing one double bond in the ring and one in the side chain (1-vinyl-3-cyclohexene, dipentene, 1-allyl-1-cyclohexene). It was established that the contact isomerization of the investigated hydrocarbons in the presence of gumbrin at 300-310° fails to lead to the formation of hydrocarbons with a conjugated system of double bonds. The catalyzates failed to react with maleic anhydride and possessed low unsaturation.

For comparison we studied the conversion of 1,3-cyclohexadiene under analogous conditions. In addition, we subjected 3-cyclohexylallylene to contact treatment, assuming that here, in accord with the scheme of Levina, there should occur preliminary isomerization of the acetylene hydrocarbon into the corresponding cyclohexadiene derivative, which will then later undergo contact transformation. It was shown that in this case also the catalyzates fail to contain either the original hydrocarbons or any hydrocarbons with a conjugated system of double bonds. After removing the unsaturated hydrocarbons the monomeric fractions of the catalyzates are, as a rule, binary mixtures of the corresponding aromatic and cyclohexane hydrocarbons, from which the individual hydrocarbons were isolated and identified from their physicochemical constants and oxidation products. In the case of dipentene and 3-cyclohexylallylene the hydrogen redistribution proceeds in accord with the equation for irreversible catalysis, and the amount of aromatic hydrocarbons in the catalyzate is twice the amount of the corresponding cyclohexane hydrocarbons. The isomerization of 1-vinyl-3-cyclohexene, 1,3-cyclohexadiene and 1-allyl-1-cyclohexene was accompanied by the formation of relatively large amounts of cyclohexane hydrocarbons, which, probably, is the result of the concurrently proceeding dehydropolymerization reaction.

It was established that the isomerization of 1,3-cyclohexadiene is accompanied by the partial transition of the six-membered ring into a five-membered one. This can be explained by the fact that the cyclohexene, formed as the result of the stepwise hydrogenation process, that runs parallel with the irreversible catalysis process, is isomerized into methylcyclopentene [8]:



EXPERIMENTAL

The contact conversion of the hydrocarbons was run by the counterflow method at 300-310° over granulated gumbrin, previously activated by heating at 350° for 4-6 hours. The passage rate for the hydrocarbons was 0.2-0.25 ml per 1 ml of contact in 1 hour. The obtained catalyzates were divided into low-boiling (monomeric) and high-boiling (polymeric) fractions. The unsaturated hydrocarbons were removed from the low-boiling fractions by treatment with 85% H_2SO_4. The amount of aromatic hydrocarbons present was determined from the physicochemical constants of the mixture [12, 13], and also by the sulfonation method. The cyclohexane hydrocarbon was separated by treatment of the mixture with 7% oleum, while the aromatic hydrocarbon was isolated from the sulfonic acids by the Kizhner method [11]. We failed to make a detailed study of the polymeric fractions.

Contact Conversion of 1-Vinyl-3-cyclohexene. The hydrocarbon was obtained by the thermal polymerization of divinyl in a bomb at 160-180°. Fractional distillation of the product gave :

b.p. 128-130°, n_D^{20} 4657, d_4^{20} 0.8323, aniline point −29°. Literature data [9]: b.p. 129.5-130.5, n_D^{20} 1.4653, d_4^{20} 0.8320.

The total amount of hydrocarbon passed over gumbrin was 166 g. The yield of catalyzate was 133 g. The increase in gumbrin weight ("coke") and escaped gases was 33 g.

Low-boiling Catalyzate Fraction: B.p. 120-150°, Br No. 71.3; aniline point −4°, n_D^{20} 1.4561, d_4^{20} 0.8475. Fails to react with maleic anhydride. Removal of the unsaturated hydrocarbons (~26%) gave a mixture, from its indices corresponding to a mixture of 66% ethylcyclohexane and 34% ethylbenzene [12]: b.p. 125-135°, n_D^{20} 1.4545, d_4^{20} 0.8103, aniline point +10°. The ethylcyclohexane (~60% by volume) was isolated by treatment of the mixture with 7% oleum.

B.p. 130-131°, n_D^{20} 1.4319, d_4^{20} 0.7838, aniline point +48.5°. Literature for ethylcyclohexane [10]: B.p. 131.78°, n_D^{20} 1.4330, d_4^{20} 0.7879, aniline point +48.3°.

The ethylbenzene was isolated from the sulfonic acids: B.p. 135-136°, n_D^{20} 1.4961, d_4^{20} 0.8671. Literature for ethylbenzene [10]: B.p. 136.19°, n_D^{20} 1.4959, d_4^{20} 0.8670.

Oxidation of the aromatic hydrocarbon with alkaline $KMnO_4$ gave benzoic acid: m.p. 120-122°; m.p. of the anilide 161-162°.

High-boiling Catalyzate Fraction: B.p. 115-130° at 5 mm (12%), n_D^{20} 1.5181, M 206, aniline point +13.6°; B.p. 135-145° at 5 mm (~68%), n_D^{20} 1.5309, M 208, aniline point −4.6°. Residue: n_D^{20} 1.5714, M 319.

Treatment of the fraction with b.p. 135-145° (5 mm) with 7% oleum gave the cycloparaffin (cycloalkane) hydrocarbon (~27%): B.p. 162° (20 mm), n_D^{20} 1.4912, d_4^{20} 0.9172, MR_D 69.49. $C_{16}H_{40}$, calculated 69.49. Aniline point +53.5°.

Contact Conversion of Dipentene. The dipentene was obtained by the thermal polymerization of isoprene in a bomb at 170-180°.

B. p. 174-175°, n_D^{20} 1.4737, d_4^{20} 0.8454, bromine number 230.5. Literature [9]: B. p. 174-175, n_D^{20} 1.47428, d_4^{20} 0.8454.

The low-boiling catalyzate fraction (~65 %) boiled in the limits 160-180° and failed to react with maleic anhydride and alcoholic SO_2 solution. Removal of the unsaturated hydrocarbons (~26%) gave a mixture, which from its indices corresponded to a mixture of 65% p-cymene and 35% methane [12]:

B. p. 162-168°, n_D^{20} 1.4699, d_4^{20} 0.8344, aniline point −1.7°. Treatment with 7% oleum resulted in the isolation of the methane (~36%).

B. p. 168-169°, n_D^{20} 1.4381, d_4^{20} 0.7977, aniline point +56.5°. Literature [10]: B. p. 170.7°, n_D^{20} 1.4395, d_4^{20} 0.8008, aniline point +56.5°.

The p-cymene was isolated from the sulfonic acids:

B. p. 175-177°, n_D^{20} 1.4914, d_4^{20} 0.8568. Literature [10]: B. p. 177.25°, n_D^{20} 1.4909, d_4^{20} 0.8573.

The oxidation with alkaline $KMnO_4$ solution gave terephthalic acid, identified as the dimethyl ester (m. p. 136°). The absorption maxima in the ultraviolet of the isolated aromatic hydrocarbon and of a specimen of chemically pure p-cymene coincided: 270, 268, 263, 260 mμ. The polymeric fractions of the dipentene catalyzate were not studied.

Contact Conversion of 1-Allyl-1-cyclohexene. The 1-allyl-1-cyclohexanol used for the preparation of the allylcyclohexene was obtained by the action of magnesium on a mixture of cyclohexanone and allyl bromide [14]: B. p. 81° (10 mm), n_D^{20} 1.4733, d_4^{20} 0.9314. The allylcyclohexanol was dehydrated with crystalline oxalic acid to give 1-allyl-1-cyclohexene:

B. p. 159-160°, n_D^{20} 1.4762, d_4^{20} 0.8438. Literature [5]: B. p. 158-159°, n_D^{20} 1.4770, d_4^{20} 0.8426.

The low-boiling catalyzate fraction (~56%) boiled at 150-160°, n_D^{20} 1.4603, d_4^{20} 0.8315, bromine number 36.5. Removal of the unsaturated hydrocarbons (~28%) gave a mixture, which from its indices corresponded to a mixture of 45% propylbenzene and 55% propylcyclohexane: n_D^{20} 1.4591, d_4^{20} 0.8207, aniline point +12°.

The propylcyclohexane (~56%) was isolated by treatment of the mixture with 7% oleum:

B. p. 154-155°, n_D^{20} 1.4367, d_4^{20} 0.7942, aniline point +50.4°. Literature [10]: B. p. 152.72°, n_D^{20} 1.4370, d_4^{20} 0.7936, aniline point +50°.

The propylbenzene, identified by its physical properties and oxidation product, was isolated from the sulfonic acids:

B. p. 157-158°, n_D^{20} 1.4916, d_4^{20} 0.8615. Literature [10]: B. p. 159.22, n_D^{20} 1.4920, d_4^{20} 0.8620.

Oxidation of the aromatic hydrocarbon with alkaline $KMnO_4$ solution gave benzoic acid: m. p. 120.5-121° (from water), m. p. of the anilide 161-162°. The polymeric fractions of the catalyzate were not studied.

Contact Conversion of 1,3-Cyclohexadiene. 1,3-Cyclohexadiene was synthesized by the Hofmann method [5]: B. p. 80-81°, n_D^{20} 1.4722, d_4^{20} 0.8407.

The contact conversion of the cyclohexadiene was accompanied by considerable "coke formation" and the evolution of gaseous products. The low-boiling catalyzate fraction (~ 60.6%) boiled in the range 60-84°, n_D^{20} 1.4540, d_4^{20} 0.8157, bromine number 56.7. The mixture obtained after removal of the unsaturated hydrocarbons had n_D^{20} 1.4582, d_4^{20} 0.8198. The qualitative reactions for benzene were positive. Its absorption maxima in the ultraviolet coincided with those for benzene: 268, 260, 256, 249, 239, 237, 233, 226 mμ.

The amount of benzene, determined by sulfonation, proved to be equal to 48.4% (by volume). Removal of the benzene left a mixture of paraffin hydrocarbons (alkanes), the constants of which were intermediate between those of methylcyclopentane and cyclohexane: B. p. 77-79°, n_D^{20} 1.4180, d_4^{20} 0.7636, aniline point +32.5°. Dehydrogenation of the mixed paraffin hydrocarbons over Pd-charcoal and subsequent treatment with 7% SO_3 gave a hydrocarbon, the indices of which were very close to those of methylcyclopentane:

B. p. 72-73°, n_D^{20} 1.4103, d_4^{20} 0.7492, aniline point +34.5°. Literature for methylcyclopentane [10]: B. p. 71-81°, n_D^{20} 1.4098, d_4^{20} 0.7486, aniline point +34.5°.

A fraction (~26.8% of the catalyzate weight) was isolated from the polymeric portion of the catalyzate, which in its properties was close to that of a mixture of dehydro- and dihydrocyclohexadiene – the usual products of the acidic polymerization of cyclohexadiene [18]: B. p. 94-105° (16 mm), n_D^{20} 1.5157, d_4^{20} 0.9670, bromine number 16.3.

Contact Conversion of 3-Cyclohexylallylene. The cyclohexylallylene was obtained in the usual manner [16]:

B. p. 60-62° (24 mm), n_D^{20} 1.4608, d_4^{20} 0.8451, MR_D 39.14. C_9H_{14} Γ_1. Calculated 39.49. Literature [17]: B. p. 55° (17 mm), n_D^{20} 1.4603, d_4^{20} 0.8440.

With $AgNO_3$ in alcohol solution this hydrocarbon gives the characteristic crystalline precipitate $C_6H_{11}CH_2C \equiv CAg \cdot AgNO_3$. The catalyzate fails to react with $AgNO_3$ and does not show other reactions for the acetylene (triple) bond. The low-boiling catalyzate fraction (~63.5%) had b. p. 146-160°, n_D^{20} 1.4672, d_4^{20} 0.8401, aniline point −3.8°, and bromine number 68.9.

Removal of the unsaturated hydrocarbons gave a mixture, the indices of which correspond to a mixture of 63.3% propylbenzene and 36.7% propylcyclohexane [12]; its boiling range 153-160°, n_D^{20} 1.4693, d_4^{20} 0.8336, aniline point 7.2°.

Treatment of the mixture with 7% oleum resulted in the isolation of propylbenzene, which was characterized: B. p. 156-157°, n_D^{20} 1.4920, d_4^{20} 0.8640. Literature [10]: B. p. 159.5°, n_D^{20} 1.4925, d_4^{20} 0.8620.

The polymeric fractions of the catalyzate (~ 36.5%) were not studied.

SUMMARY

1. The contact conversion on gumbrin of cyclohexene hydrocarbons with unsaturated side chains leads to the formation of mixtures of cycloparaffin and aromatic hydrocarbons, together with polymerization products.

2. 1,3-Cyclohexadiene and 3-cyclohexylallylene suffer similar transformations under these conditions, which serves to support the scheme proposed by R. Ya. Levina for the mechanism of the contact isomerization of such hydrocarbons.

3. Together with hydrogen redistribution by the irreversible catalyzate reaction there is also hydrogenation taking place, the latter being due to the hydrogen that is evolved in the concurrently proceeding dehydropolymerization process.

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QUATERNARY AMMONIUM SALTS

II. DEHYDROCHLORINATION

A. T. Babayan and I. Ya. Zurabov

In working with amines and quaternary ammonium salts, containing the 3-chloro-2-butenyl radical, our attention was drawn to the clearly expressed relationship existing between the reaction rate of their dehydrochlorination and the character of the nitrogen. Thus, for example, for the dehydrochlorination of amines it is necessary to boil for many hours with alcoholic potassium hydroxide [1]. On the other hand the quaternary ammonium salts, obtained from these same amines, when heated with aqueous sodium hydroxide solution suffer rapid and quantitative cleavage with the formation of the tertiary amine and a mixture of chloroprene and monovinylacetylene [2]. The presence of the latter in the reaction products shows that, together with cleavage, there is also some partial dehydrochlorination occurring here. The dialkylbutynylamine is obtained if two 3-chlorobutenyl radicals are present. This clearly indicates that dehydrochlorination proceeds, not simultaneously with the cleavage of the ammonium compound, but instead precedes it. The tetrasubstituted ammonium salts studied by us, containing the 3-chlorobutenyl radical, suffer alkaline cleavage at temperatures above 70-75°. It could be hoped that if definite temperature conditions were observed for the reaction that it would be possible to realize dehydrochlorination without disturbing the integrity of the tetrasubstituted ammonium complex. The first experiments revealed that the dehydrochlorination of these quaternary ammonium compounds proceeds with considerable speed even without heating. The degree of dehydrochlorination was judged by the amount of halide ions in solution. The experimental results are given in the table. As can be seen from the table, the rate for the dehydrochlorination of the different studied quaternary ammonium salts is of the same order. Even in the first hour of reaction more than 60 % of the salt suffers dehydrochlorination. The influence of the radicals, entering into the composition of the ammonium complex, is perceptible, but it fails to essentially change the picture. Under analogous conditions the amines, containing the 3-chlorobutenyl radical, prove to be completely inert to dehydrochlorination.

The ability of the tetrasubstituted ammonium salts studied by us to be easily dehydrochlorinated at temperatures that are still insufficient for cleavage makes it possible to direct the above described reaction for the alkaline cleavage of these salts [2] toward the formation of pure monovinylacetylene, without chloroprene as impurity. When two 3-chlorobutenyl radicals are present this reaction can be used for the preparation of dialkylbutynylamines by the following scheme, without contamination by the dialkyl-3-chlorobutenylamine:

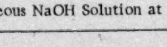
$$R_2N\begin{matrix}CH_2CH{=}CClCH_3\\ |\\ Cl\\ |\\ CH_2CH{=}CClCH_3\end{matrix} \xrightarrow[60-65^\circ]{NaOH} R_2N\begin{matrix}CH_2{-}C{\equiv}C{-}CH_3\\ |\\ OH\\ |\\ CH_2{-}C{\equiv}C{-}CH_3\end{matrix} \xrightarrow{Heat}$$

$$\rightarrow R_2N{-}CH_2{-}C{\equiv}C{-}CH_3 + CH_2{=}CH{-}C{\equiv}CH.$$

The dialkylbutynylamines, and also the monovinylacetylene, are obtained sufficiently pure and in high yields.

TABLE

Action of 20% Aqueous NaOH Solution at 55° (Time 1 Hour)

Compound Formula	Molar Ratio of compound to caustic	Amount of halide ion (in gram-atoms per 1 mole of compound)
	1:4	2.48
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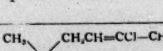
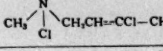
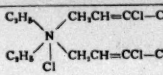
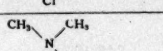
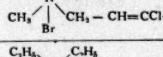
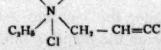
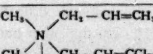
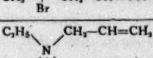
	1:4	2.15
	1:3	1.335
	1:3	1.718
	1:3	1.678
	1:3	1.644
	1:1	1.63
	1:3	0.00
	1:1	0.00

* Heating 3 hours, 55°.

** Heating for 1 hour on the boiling water bath.

EXPERIMENTAL

Dehydrochlorination of Dimethyl-di-(3-chlorobutenyl) Ammonium Chloride. To 0.02 mole of the tetrasubstituted ammonium salt was added the corresponding molar amount of caustic solution. The mixture was thoroughly mixed until solution had been achieved and then was allowed to stand at predetermined temperatures. Then the reaction mixture was diluted with distilled water to either 50 or 100 ml, and the amount of halide ion was determined by precipitation with silver nitrate solution. The experiments on the dehydrochlorination of the remaining salts, and also of the amines, were run in similar manner.

Preparation of Monovinylacetylene and Dimethylbutynylamine. A mixture of 27 g of dimethyl(3-chlorobutenyl) amine, 25 g of 1,3-dichloro-2-butene and 25 g of water was stirred in a flask, fitted with reflux condenser, stirrer and dropping funnel. In the absence of water the tetrasubstituted salt is formed with explosive force and part of the liquid is ejected from the flask. In the presence of water, with stirring, the reaction mixture can even be heated to accelerate the process. The lower water layer increases in measure with quaternary salt formation and at the end the whole mass is converted into a clear, slightly colored solution. Then to the reaction mixture was added 32 g of sodium hydroxide as a 40% aqueous solution. With

continued stirring the mixture was heated at 60-65° for 2 hours, and then on the boiling water bath. The monovinylacetylene that was formed escaped through the reflux condenser, cooled with tap water (12-13°), and was condensed in a coil receiver at −25 to −30°. After the evolution of gas had ceased the reflux condenser was replaced by a straight condenser, and the amine was distilled from the reaction mixture. At first the amine distilled with a small amount of water, and then water distilled. The amine was salted out with potassium hydroxide, dried over potassium hydroxide lumps, and distilled. The amount of amine (in moles) in each fraction was determined by titration. First fraction, 85-110°, 0.0336 mole (4.0 g); 2nd fraction, 110-117°, 0.1250 mole (12.3 g); 3rd fraction, 117-135°, 0.0250 mole (3.0 g). The total was 0.1846 mole of amine (91.8%).

The 1st fraction, judging by the analysis, contains traces of moisture and is possibly chloroprene; the 2nd fraction is almost completely pure dimethylbutynylamine; the 3rd fraction contains 1.735 g of dimethyl(3-chlorobutenyl)amine (6.8%). As a result, the yield of dimethylbutynylamine is 85%. The yield of monovinylacetylene was 7.4 g (71%). About 1 g of polymerized brittle mass was extracted from the reaction flask.

SUMMARY

1. It was established that quaternary ammonium salts, containing the 3-chloro-2-butenyl radical, are easily dehydrochlorinated.

2. A laboratory method was presented for the preparation of monovinylacetylene.

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OXYDOL SERIES

VII. PREPARATION AND PROPERTIES OF PHENYL-SUBSTITUTED α,β- AND β,γ-ALCOHOL OXIDES

V. I. Pansevich-Kolyada, V. A. Ablova and L. A. Kureichik

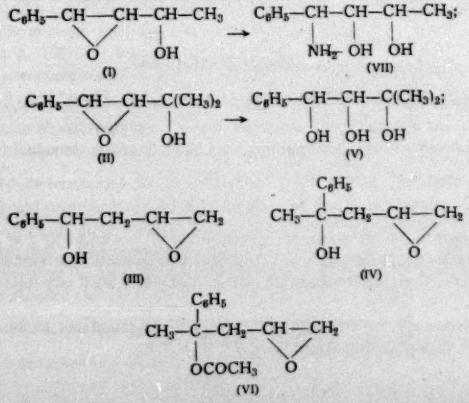
In previous communications [1, 2] it was shown that the α,β-alcohol oxides of the aliphatic series, containing the tertiary alcohol group and a tri-substituted oxide ring, under the influence of anhydrous zinc chloride and aqueous mineral acid solutions, are cleaved with the formation of carbonyl compounds, and a mechanism was postulated for this reaction. For the alcohol oxides studied by us the usual products were isobutyraldehyde and the corresponding ketones.

An even easier cleavage is described for a number of phenyl-substituted α,β-alcohol oxides, which are cleaved under the influence of the acidic reagents contained in laboratory air [3-5], or when kept in a desiccator over water-removing agents, with the formation of acetophenone and isobutyraldehyde [6].

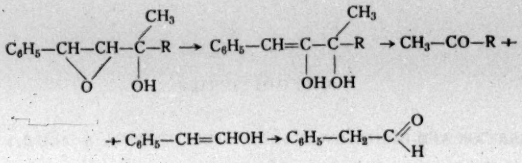
In contrast to the alcohol oxides described by us, only the 1-phenyl-1,2-epoxy-3-butanol and 1-phenyl-1,2-epoxy-3-pentanol [7] failed to be cleaved, but instead underwent hydration with the formation of substituted glycerols, in water that contained several drops of concentrated sulfuric acid. The last two alcohol oxides differed from the previous ones in their structure, which, undoubtedly, also showed up their properties.

It was of interest to establish to what degree the reaction for the cleavage of α,β-alcohol oxides in the presence of zinc chloride and mineral acids is general for them, and also to establish the behavior of the β,γ-alcohol oxides toward these substances.

In this study we oxidized trans-methylstyrylcarbinol, dimethylstyrylcarbinol, allylphenylcarbinol and methylallylphenylcarbinol with acetyl hydroperoxide and obtained two α,β-alcohol oxides, 1-phenyl-1,2-epoxy-3-butanol (I) and 3-methyl-1,2-epoxy-3-butanol (II), and two β,γ-alcohol oxides, 1-phenyl-3,4-epoxy-1-butanol (III) and 2-phenyl-4,5-epoxy-2-pentanol (IV), and we also studied the behavior of these alcohol oxides toward anhydrous zinc chloride, aqueous sulfuric acid solution, acetic anhydride and ammonia.



When 1-phenyl-1, 2-epoxy-3-butanol (I) and 3-methyl-1-phenyl-1, 2-epoxy-3-butanol (II) are heated with either anhydrous $ZnCl_2$ or in 0.1 % sulfuric acid solution both of the alcohol oxides, the same as the α, β-oxydols of the aliphatic series, are cleaved into phenylacetaldehyde and respectively acetaldehyde and acetone:



$$+ C_6H_5{-}CH{=}CHOH \rightarrow C_6H_5{-}CH_2{-}C(=O)H$$

R = H and CH_3.

The alcohol oxide dimethylstyrylcarbinol (II), under the conditions described by T. I. Temnikova and V. F. Martynov [7], suffers hydration with the formation of 3-methyl-1-phenyl-1, 2, 3-butanetriol (V). Our two attempts to hydrate the oxide of trans-methylstyrylcarbinol under these conditions proved unsuccessful; only cleavage took place, the same as in 0.1 % sulfuric acid solution.

Such a difference in the behavior of the methylstyrylcarbinol oxides that were studied by Temnikova and Martynov [7] and by us is explained, apparently, by the fact that we did our work with two different steoreoisomers of this alcohol oxide. It was shown by T. I. Temnikova and V. A. Kropacheva on the example of tert-butyl styryl ketone oxide that the cis- and trans- forms of the α-oxides possess different properties.

In contrast to the α, β-alcohol oxides, the β, γ-alcohol oxides with either zinc chloride or with aqueous mineral acid solutions fail to undergo cleavage and instead give condensation products. When heated with acetic anhydride the phenyl-substituted oxydols form unstable compounds. Only in the case of 2-phenyl-4, 5--epoxy-2-pentanol (IV) was the epoxy acetate isolated, namely 2-phenyl-2-acetoxy-4, 5-epoxypentane (VI).

Viscous undistillable substances are formed when the phenyl-substituted alcohol oxides are heated with aqueous ammonia solution. These substances fail to crystallize and do not give crystalline hydrochlorides; tar-formation occurred when these substances were treated with dry hydrogen chloride in either alcohol or ether medium. Only in the case of the methylstyrylcarbinol oxide was the amino glycol isolated, which, most probably, is 1-phenyl-1-amino-2, 3-butanediol (VII).

As a result, the results obtained by us show that the phenyl-substituted α, β- and β, γ-alcohol oxides are quite different from each other. The oxide ring of the α, β-alcohol oxides is unstable and as a result of this the α, β-alcohol oxides are easily cleaved and react with different reagents. On the other hand, the β, γ-alcohol oxides are characterized by considerable inertness and, may be condensed only under extreme conditions.

EXPERIMENTAL

Preparation of trans-Methylstyrylcarbinol Oxide (1-Phenyl-1, 2-epoxy-3-butanol) (I)

The alcohol oxide was obtained by the oxidation of trans-methylstyrylcarbinol with acetyl hydroperoxide, the carbinol having been prepared from methylmagnesium chloride and cinnamaldehyde [9].

B. p. 119-121° (6 mm), n_D^{20} 1.5698, d_4^{20} 1.0168, MR_D 47.73; calculated 45.84.
Found %: C 81.19; H 8.30. $C_{10}H_{12}O$. Calculated %: C 81.08; H 8.10.

To 41 g of the alcohol in 100 ml of anhydrous ether at 20-25° was added 23 g of acetyl hydroperoxide (94%). The reaction proceeded smoothly. The oxidation products were worked up as described earlier [1] and then vacuum-distilled. There was obtained 33 g of substance as a thick oily liquid of slightly yellowish-green color.

B. p. 122-123° (2 mm), n_D^{20} 1.5330, d_4^{20} 1.0938, MR_D 46.53 calculated 45.88.
Found % : C 73.35; H 7.38. $C_{10}H_{12}O_2$. Calculated % : C 73.17; H 7.31.

Cleavage of 1-Phenyl-1, 2-epoxy-3-butanol in Sulfuric Acid Solution. To 10 ml of water, containing 3 drops of concentrated sulfuric acid, was added 3.2 g of the alcohol oxide. The mixture was heated for 2 hours on the boiling water bath. The volatile substances were trapped in dimedone solution, from which, after heating on the water bath, crystals were obtained with m.p. 138-139°. The mixed melting point with the adduct from dimedone and acetaldehyde failed to show a depression. The nonvolatile products were extracted from the aqueous solution with ether and dried over $MgSO_4$. Removal of the ether by distillation left as residue a thick yellow oil with an aromatic aldehyde odor. Two-hour heating of this oily substance with dimedone in aqueous-alcohol solution gave a crystalline product with m.p. 163-164°, which corresponds to the adduct of dimedone with phenylacetaldehyde [10].

Cleavage of 1-Phenyl-1, 2-epoxy-3-butanol Under the Influence of Zinc Chloride. To 2.2 g of the alcohol oxide was added 0.8 g of fused zinc chloride. A slight temperature rise was observed. The mixture was heated on the water bath. The volatile substances were trapped in dimedone solution, where crystals of the acetaldehyde adduct with m.p. 138° were obtained. The zinc chloride was dissolved in water, and the oily residue was extracted with ether. When heated with dimedone in aqueous-alcohol solution this residue gave crystals of the phenylacetaldehyde adduct with m.p. 163°.

Reaction of 1-Phenyl-1, 2-epoxy-3-butanol With Ammonia. To 5.0 g of the alcohol oxide was added a 5-fold amount of 25% aqueous ammonia solution. The mixture was heated in a sealed glass tube for 6 hours on the boiling water bath. The oxydol dissolved completely. There was no pressure when the tube was opened. Evaporation of the solution in vacuo gave fine crystals, which after recrystallization from alcohol melted at 130-132°. They are readily soluble in dilute hydrochloric acid, insoluble in ether, petroleum ether and hexane, and difficulty soluble in benzene. The test for nitrogen was positive.

Found %: C 66.26; H 8.79; N 7.59. $C_{10}H_{15}O_2N$. Calculated %: C 66.30; H 8.28; N 7.73.

Preparation of Dimethylstyrylcarbinol Oxide (3-Methyl-1-phenyl-1, 2-epoxy-3-butanol) (II)

The alcohol oxide was obtained by the oxidation of dimethylstyrylcarbinol with acetyl hydroperoxide, the carbinol having been prepared by the Grignard reaction from methylmagnesium chloride and benzylideneacetone [12].

B.p. 114-115° (4 mm), n_D^{20} 1.5644, d_4^{20} 0.9952, MR_D 52.98; calculated. 50.45.
Found %: C 80.97; H 8.24. M 161.5, 167.5. $C_{11}H_{14}O$. Calculated %: C 81.48; H 8.33, M 162.

To 50 g of the alcohol in 100 ml of anhydrous ether at 20-25° was added 25 g of acetyl hydroperoxide (96%). The reaction proceeded smoothly. After 10 days the reaction products were worked up in the usual manner and vacuum-distilled. There was obtained 27 g of thick yellowish liquid, soluble in the different organic solvents.

B.p. 108-110° (4 mm), n_D^{20} 1.5340, d_4^{20} 1.0577, MR_D 52.30; calculated 50.49.
Found % C 75.20; H 7.90; OH 9.88. M 174.0, 180.3. $C_{11}H_{14}O_2$. Calculated %: C 74.16; H 7.86; OH 9.55 M 178.

Repeated distillations failed to improve the analysis results. Apparently, the alcohol oxides undergo partial change when distilled.

Cleavage of 3-Methyl-1-phenyl-1, 2-epoxy-3-butanol in Aqueous Sulfuric Acid Solution. To 10 ml of water was added 3 drops of concentrated sulfuric acid and 2.0 g of the alcohol oxide. The mixture was heated on the boiling water bath. The volatile products were trapped in semicarbazide solution, in which after several days the acetone semicarbazone with m.p. 186-187° was obtained [10]. After heating with dimedone solution, the nonvolatile substance with the odor of phenylacetaldehyde gave the adduct with m.p. 163-165° [10].

Cleavage of 3-Methyl-1-phenyl-1, 2-epoxy-3-butanol Under the Influence of Zinc Chloride. To 2 g of the alcohol oxide was added 0.8 g of zinc chloride, and the mixture was heated on the water bath. The zinc chloride was dissolved in water, while the oily product with dimedone gave the crystalline dimedone-phenylacetaldehyde adduct with m.p. 162-165°.

Hydration of 3-Methyl-1-phenyl-1, 2-epoxy-3-butanol. To 100 ml of water was added 5 drops of concentrated sulfuric acid and 1.0 g of the alcohol oxide. The alcohol oxide dissolved under shaking. The mixture was warmed slightly on the water bath. The reaction product was salted out with NaCl, repeatedly extracted with ether, and dried over $MgSO_4$. Removal of the ether by distillation gave 0.5 g of crystals, which after recrystallization from a petroleum ether-benzene mixture melted at 91-92°.

Found %: C 67.94; H 7.49. $C_{11}H_{16}O_3$. Calculated %: C 67.34; H 8.16.

The analysis data correspond to 1-phenyl-3-methyl-1, 2, 3-butanetriol.

Preparation of Allylphenylcarbinol Oxide (1-Phenyl-3,4-epoxy-1-butanol (III)

The alcohol oxide was obtained by the oxidation of allylphenylcarbinol with acetyl hydroperoxide, the carbinol having been synthesized from allylmagnesium bromide and benzaldehyde [11, 12].

B.p. 116-119° (13 mm), n_D^{20} 1.5322, d_4^{20} 1.0090, MR_D 45.46; calculated. 45.83.
Found %: C 81.09; H 8.05. $C_{10}H_{12}O$. Calculated %: C 81.08; H 8.10.

To 34.0 g of the alcohol in 70 ml of ether at 20-25° was added 18 g of the hydroperoxide (94%). The reaction was very slow. After 8 days the reaction products were worked up in the usual manner. When they were vacuum-distilled there was obtained 17 g of thick yellowish-green liquid, which proved to be the alcohol oxide (III).

B.p. 138-139° (2 mm), n_D^{20} 1.5349, d_4^{20} 1.1140, MR_D 45.82; calculated. 45.88.
Found %: C 73.51; H 7.30; OH 9.69. M 181.3. $C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.31; OH 10.35. M 164.

The allylphenylcarbinol entered into reaction with acetic anhydride, ammonia and zinc chloride, but we were unable to isolate the products of these reactions.

Preparation of Methylallylcarbinol Oxide (2-Phenyl-4,5-epoxy-2-pentanol) (IV)

The alcohol oxide was obtained by the oxidation of methylallylphenylcarbinol with acetyl hydroperoxide, the carbinol having been synthesized from allylmagnesium bromide and acetophenone [11]. At the end of reaction the flask contents were heated for 1 hour on the water bath. The complex was decomposed with ice and NH_4Cl solution. The ether solution was dried over K_2CO_3 and the alcohol was distilled; B.p. 104-105° (15 mm) [12].

To 37.5 g of 2-phenyl-4-penten-2-ol in 80 ml of anhydrous ether was added 17.5 g of acetyl hydroperoxide. The oxidation proceeded very slowly with hardly any evolution of heat. After 9 days the reaction products were worked up as in the previous experiments and after drying over $MgSO_4$, were vacuum-distilled. The yield of oily liquid was 17 g.

B.p. 132° (1.5 mm), n_D^{20} 1.5318, d_4^{20} 1.1066, MR_D 49.86; calculated 50.49.
Found %: C 73.80; H 7.84; OH 10.63. M 163.2, 181.9. $C_{11}H_{14}O_2$. Calculated %: C 74.16; H 7.80; OH 8.50; M 178.

Reaction of 2-Phenyl-4,5-epoxy-2-pentanol With Acetic Anhydride. A mixture of 5 g of the alcohol oxide and 15 g of acetic anhydride was boiled for 4 hours. The mixture failed to show darkening. Vacuum-distillation gave 2 g of substance.

B.p. 162-163° (7 mm), n_D^{20} 1.5062, d_4^{20} 1.0925 MR_D 59.90; calculated. 59.86
Found %: C 70.08; H 7.25; OH 1.11. M 195.9. $C_{13}H_{16}O_3$. Calculated %: C 70.90; H 7.50; OH 0. M 207.

The substance contained an impurity showing the presence of active hydrogen.

Action of Zinc Chlorides on 2-Phenyl-4,5-epoxy-2-pentanol. To 12 g of the alcohol oxide was added 2.0 g of pulverized anhydrous zinc chloride and the mixture was heated for 2 hours on the boiling water bath. The mixture turned dark-red and viscous. The zinc chloride was dissolved in water, while the substance was extracted with ether and after drying over $MgSO_4$, was vacuum-distilled. The yield of substance was 4 g.

B.p. 130-132° (1 mm), n_D^{20} 1.5338, d_4^{20} 1.1056, MR_D 50.04; calculated. 50.49.
Found %: OH 10.17. $C_{11}H_{14}O_2$. Calculated %: OH 9.50.

The alcohol oxide was recovered unchanged. The high-boiling products underwent decomposition when distilled at 1 mm.

SUMMARY

1. Acetyl hydroperoxide was used to oxidize methylstyrylcarbinol, dimethylstyrylcarbinol, allylphenylcarbinol and methylallylphenylcarbinol.

2. Four phenyl-substituted alcohol oxides were obtained. Of them two were α,β-alcohol oxides, namely 1-phenyl-1,2-epoxy-3-butanol and 3-methyl-1-phenyl-1,2-epoxy-3-butanol, and two were β,γ-alcohol oxides, namely 1-phenyl-3 4-epoxy-1-butanol and 2-phenyl-4,5-epoxy-2-pentanol.

3. The oxide ring of the α,β-alcohol oxides is easily modified, as a result of which the α,β-alcohol oxides undergo cleavage in acid medium, and also enter into reaction with different reagents.

The β, γ-alcohol oxides are characterized by considerable inertness, and undergo condensation if drastic conditions are employed.

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ACTION OF NITRIC ACID ON METHYLOL DERIVATIVES OF 4-ETHYLPYRIDINE

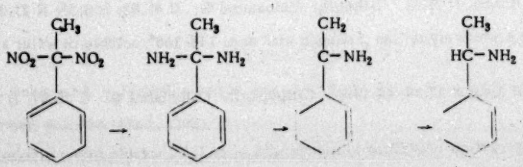
M. V. Rubtsov, E. S. Nikitskaya and V. S. Usovskaya

As was shown earlier [1], the methylol derivatives of γ-picoline are easily oxidized by nitric acid to isonicotinic acid. It appeared of interest to us to elucidate the possibility of obtaining isonicotinic acid by the oxidation of the methylol derivatives of 4-ethylpyridine with nitric acid. For our work we used both the mono- and dimethylol derivatives, and also their mixture, which was formed in the condensation of 4-ethylpyridine with formalin and which consisted of 75% of the dimethylol and 25% of the monomethylol derivatives.

The experiments made by us revealed that the oxidation of the methylol derivatives of 4-ethylpyridine, either as individual compounds or as their mixtures, with nitric acid, leads to the formation, together with isonicotinic acid (20%), of a considerable amount of substance (30%), which, judging from its analysis, is dinitroethylpyridine. Variation in the reaction conditions (change in the temperature and nitric acid concentration) and the use of catalysts (cerium oxalate, manganese dioxide, mercury acetate) lead to a very slight change in the obtained proportions of these compounds. Only when the mixture is oxidized with mixed acid in 25% hydrogen peroxide medium is there a considerable increase in the yield of isonicotinic acid with a simultaneous reduction in the yield of the dinitroethylpyridine.

The reduction of the dinitroethylpyridine with hydrogen in the presence of skeletal nickel catalyst leads to the formation, together with the evolution of free ammonia, of 4-(α-aminoethyl) pyridine, the identity of which was established by comparing it with the compound obtained by the reduction of 4-acetylpyridine oxime.

The cleavage of one amino group in the reduction of the dinitro compound is evidence that both of the nitro groups are bound to the same carbon atom, and, consequently, the starting dinitro compound has the structure of 4-(α,α-dinitroethyl) pyridine. The process for its conversion into the (aminoethyl) pyridine can be depicted by the following scheme:



In studying the structure of the (aminoethyl) pyridine we encountered the necessity of obtaining the oxime of 4-acetylpyridine. A melting point of 142° is given for this compound in the literature [2], while the 4-acetylpyridine oxime synthesized by us melted in the range 120-158°. Repeated recrystallization of this substance from benzene gave two compounds — one with m.p. 121-123° and the other with m.p. 157-159°. Based on the elementary analysis, both of the compounds correspond to the composition of the 4-acetylpyridine oxime and apparently are the cis- and trans- isomers. Apparently, the 4-acetylpyridine oxime described in the literature is a mixture of these isomers.

The reduction of the individual isomers with hydrogen in the presence of palladium catalyst yields, the same as when their mixture is reduced, 4-(α-aminoethyl) pyridine.

EXPERIMENTAL

Methylol Derivatives of 4-Ethylpyridine. The method proposed by R. Lukas and J. Ernest [3] for the preparation of the dimethylol derivative of 4-ethylpyridine is characterized by being exceedingly long, for which reason we prepared the methylol derivatives by the same method as was described earlier [1] for the preparation of the methylol derivative of 4-methylpyridine.

A mixture of 5.35 g of 4-ethylpyridine and 18 g of 33% formalin was heated at the boil for 15 hours, after which the excess formalin was steam-distilled, while the aqueous solution was evaporated in vacuo to a volume of 12 ml. An aqueous solution of the mixed methylol derivatives of 4-ethylpyridine was obtained, containing about 75% of the dimethylol derivative and about 25% of the monomethylol derivative. This mixture can be used directly for oxidation. To obtain the individual methylol derivatives the aqueous solution of the mixture was evaporated in vacuo, anhydrous alcohol was added twice with subsequent removal by distillation each time, and then the residue was dried in vacuo for 1 hour at 100°. The resulting syrupy mass partially crystallized when rubbed with a rod. The crystalline precipitate, being the dimethylol derivative of 4-ethylpyridine, was repeatedly washed with dry ether and then crystallized from alcohol. M.p. 93-95° [3]. Yield 5.47 g (65.5%).

The ether mother liquors were combined, the ether evaporated, and the residue was vacuum-distilled. A colorless syrupy liquid with b.p. 117° (0.35 mm) is obtained, soluble in water and in organic solvents. Yield 1.84 g (26.6%).

Found %: C 69.49; H 8.05; N 9.94. $C_8H_{11}ON$. Calculated %: C 70.07; H 8.02; N 10.21.

Oxidation of the Mixed Methylol Derivatives of 4-Ethylpyridine. To the aqueous solution of the above obtained mixture of 4-ethylpyridine methylol derivatives (12 ml), heated to 96-100°, with stirring over a period of 20-25 minutes were simultanesouly added 66 g of 25% hydrogen peroxide and 56.8 g of mixed acid (92.8%). On conclusion of addition (or toward the end of addition) the reaction mass was brought to a boil and the stormy evolution of nitrogen oxides began, which ceased after 7-10 minutes. After this the reaction mass was heated at 100-110° for 5 hours until the evolution of the nitrogen oxides had ceased completely. The resulting clear light-yellow solution was cooled to 17-20° and then neutralized by adding 40-42 g of soda of slightly acid reaction to Congo (pH~ 3.6).

The mixed precipitates of isonicotinic acid and nitro product was filtered, washed with water, and dried. The dry mixture was stirred with 20-25 ml of ether, again filtered, and the precipitate on the filter washed with 15 ml of ether and then dried at room temperature. The yield of isonicotinic acid with m.p. 306-308° (in a sealed capillary) was 3.3 g (53.6%). The ether filtrates were combined, treated with charcoal, filtered, and evaporated. There was obtained 0.65 g of nitro product as coarse colorless crystals with m.p. 55-57°, soluble in the ordinary organic solvents and insoluble in water.

Found %: C 42.78; H 3.65; N 21.21. $C_7H_7O_4N_3$. Calculated %: C 42.63; H 3.55; N 21.39.

The hydrochloride is a white crystalline substance with m.p. 148-150°, soluble in water and alcohol, and insoluble in ether.

Found %: C 36.09; H 3.43; N 17.50; Cl 14.93. $C_7H_8O_4N_3Cl$. Calculated %: C 35.97; H 3.42; N 17.98; Cl 15.20.

The picrate is a bright-yellow crystalline substance with m.p. 137°, soluble in hot alcohol, and insoluble in ether, acetone and water.

Found %: C 36.30; 36.64; H 2.42; 2.52. $C_{13}H_{10}O_{11}N_6$. Calculated %: C 36.62; H 2.34.

Reduction of 4-(α,α-dinitroethyl)pyridine. A solution of 19.7 g of 4-(α,α-dinitroethyl)pyridine in 200 ml of ethyl alcohol was hydrogenated at room temperature, in the presence of 20 g of skeletal nickel catalyst, at 40-60 mm of water pressure. The hydrogen absorption stopped after 96 hours. On conclusion of hydrogenation the catalyst was filtered (the reaction mass smells strongly of ammonia), washed with water, and the alcohol filtrates were combined and evaporated in vacuo. The residue was distilled. The yield of colorless oily substance, rapidly turning yellow in the air and with b.p. 78-80° (0.5 mm), was 10.35 g (84.8%).

Found %: C 67.75; H 8.23; N 21.75. $C_7H_{10}N_2$. Calculated %: C 67.86; H 8.19; N 22.13.

The dihydrochloride is a white crystalline substance with m.p. 235-237°, soluble in water and hot alcohol, and insoluble in ether.

Found %: Cl 36.64, 36.52. $C_7H_{12}N_2Cl_2$. Calculated %: Cl 36.41.

Preparation of 4-Acetylpyridine Oxime. 4-Acetylpyridine (9.84 g) [4] was added under stirring to a mixture of 7.34 g of potassium carbonate and 5.01 g of hydroxylamine hydrochloride in 60 ml of water. The precipitate obtained here was extracted with ether, the ether extract dried over calcined potash, and the ether distilled off. The residue was recrystallized from benzene. The yield of glistening white crystals with m.p. 120-158° was 9.0 g (92%). Repeated recrystallization of the substance with m.p. 120-158° from benzene gave two compounds – with m.p. 121-123° (soluble in boiling benzene, 1:10) and with m.p. 157-159° (soluble in boiling benzene, 1:35).

Analysis of the compound with m.p. 121-123°. Found %: C 61.94; H 5.92; N 20.23. $C_7H_8ON_2$. Calculated %: C 61.77; H 5.88; N 20.58.

Analysis of the substance with m.p. 157-159°. Found %: C 61.79; H 5.99; N 20.55.

Reduction of 4-Acetylpyridine Oxime. A solution of 5 g of the oxime with m.p. 120-158° in 100 ml of ethyl alcohol was hydrogenated at room temperature in the presence of 1 g of palladium chloride, dissolved in 13 ml of concentrated hydrochloric acid, at 40-60 mm of water pressure. The hydrogen absorption stopped after 8 hours. The catalyst was filtered, washed with alcohol, the alcohol mother liquors evaporated in vacuo, the residue treated with an excess of 50% potash solution, and extracted with ether. After drying and distilling off the ether, the residue was vacuum-distilled. The yield of colorless oily substance with b.p. 75° (0.4 mm) was 3.6 g (80.3%). The same substance and in similar yield was also obtained when each of the isomers was hydrogenated separately.

The dihydrochloride is a white crystalline substance with m.p. 235-237°, soluble in water and in hot alcohol. Its mixed melting point with the hydrochloride of the amine obtained in the reduction of 4-(α,α-dinitroethyl) pyridine failed to be depressed.

Found %: Cl 36.74. $C_7H_{12}N_2Cl_2$. Calculated %: Cl 36.41.

SUMMARY

1. The oxidation of the mixed methylol derivatives of 4-ethylpyridine with nitric acid leads to the formation of both isonicotinic acid and 4-(α,α-dinitroethyl) pyridine.

2. The reduction of 4-(α,α-dinitroethyl) pyridine with hydrogen in the presence of skeletal nickel catalyst results in the cleavage of one nitro group as ammonia and the formation of 4-(α-aminoethyl) pyridine. The structure of this compound was established by its synthesis from 4-acetylpyridine oxime.

3. The treatment of 4-acetylpyridine with an alkaline hydroxylamine solution yields a mixture of isomeric oximes, which mixture can be separated on the basis of the isomers having different solubilities in boiling benzene.

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SYNTHESES WITH ACRYLONITRILE

XXIV. STUDY OF THE COMPARATIVE REACTIVITY OF ACRYLONITRILE WITH OTHER α,β-UNSATURATED NITRILES

V. G. Yashunsky, A. P. Terentyev and V. I. Shvedov

While the chemistry of acrylonitrile has been studied quite extensively and in much detail, the information available on its closest homologs and analogs has been only fragmentary, very limited and as a rule unsystematic. It appeared of interest to us to study on the basis of a number of reactions the comparative reactivity of substituted α,β-unsaturated nitriles when compared with that of acrylonitrile, and also with each other, and in that way elucidate the influence of substituents on the ability of the double bond in these compounds to undergo addition. As subjects for study we took the α,β-unsaturated nitriles, showing different degrees of substitution by hydrocarbon radicals, and namely: acrylonitrile, methacrylonitrile, crotononitrile, β,β-dimethylacrylonitrile, cyclohexylideneacetonitrile, and the nitriles of 1-cyclohexenecarboxylic and cinnamic acids.

In this communication we present the results of our experiments on the reaction of these nitriles with glycocoll (glycine) and on their reduction with sodium in alcohol (by the Vyshnegrad method).

We selected glycine (as its potassium salt) as a typical amino compound for the reason that its use made it possible to determine the reaction results by an analytical method that did not require the separation and isolation of the reaction products from the complex reaction mixture. The method developed by us jointly with P. E. Butskus [1] for the quantitative determination of acrylonitrile in technical mixtures, at the base of which lies the reaction of the latter with glycine (in salt form), with some modifications was used to study the reaction of glycine with other α,β-unsaturated nitriles.

All of the experiments were run the same: after a weighed sample of the nitrile being studied was vigorously shaken for a predetermined length of time with a standard solution of potassium glycinate in water the excess amino acid, failing to react, was determined gasometrically by the Van Slyke method.

The nitrile and glycine were always reacted using a constant molar ratio of nitrile: glycine = 2: 5; here, depending on the molecular weight of the nitrile, the amount of nitrile taken was about 0.1-0.2 g.

The microdetermination apparatus, built by P. G. Ioanisiani [2], was used for the gasometric determination of the glycine amino group.

Since under the conditions chosen by us the addition of acrylonitrile to glycine is quantitative (100%) in 1 hour [1], then for the other unsaturated nitriles we also set a reaction time of 1 hour. In addition, a number of experiments were made at 2 hours. By doing this we obtained a comparative characterization of the reactivity shown by α,β-unsaturated nitriles for addition to a primary amino group, which permits making a comparison of the relative reaction rates of nitriles with glycine under the same conditions.

Acrylonitrile, as was to be expected, proved to be the most active of the unsaturated nitriles studied by us. As was already indicated, it shows 100% reaction with glycine in 1 hour. Of the other nitriles only the crotononitrile reacted with glycine with appreciable speed (14% in 1 hour and 23% in 2 hours, based on the nitrile). Of interest is the fact that allyl cyanide, the use of which in certain cases instead of acrylonitrile gives better results, under our conditions proved to be less reactive than the crotononitrile. The crotononitrile with which we were working was rich in the cis-isomer.

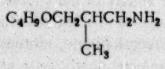
The other substituted nitriles entered into reaction but slightly, in which connection the nitrile of cinnamic acid proved to be extremely passive. After 2 hours it reacted with glycine by less than 5%. The methacrylonitrile also enters into the reaction with great difficulty (5% after 2 hours). The cyclohexylideneacetonitrile and the nitrile of 1-cyclohexenecarboxylic acid gave approximately the same results: the addition after 2 hours was 8%.

The second reaction, used by us to study the comparative reactivities of unsaturated nitriles, was the Vyshnegrad reduction method.

As we had established earlier [3], the reduction of acrylonitrile with sodium in alcohol yields two amines, namely propylamine and a γ-alkoxypropylamine, the latter containing the alkoxy group of the alcohol in which the reduction was run. The presence of two concurrent reactions gave basis to postulate that this reaction is of interest for studying the influence of substituents on the reactivity of the double bond in α,β-unsaturated nitriles.

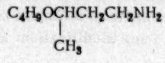
All of the nitriles were reduced under the same conditions in n-butyl alcohol. The temperature and reaction time were kept constant in all of the experiments. The components were also always taken in the same molar proportions: nitrile: alcohol: sodium = 1: 40: 10. The nitrile (0.075-0.120 mole) was dissolved in the butyl alcohol, and added to the sodium, found molten in boiling toluene. After violent reaction had ceased, when all of the metal had reacted completely, the mixture was decomposed with water and then distilled with superheated steam. The distillate was collected in hydrochloric acid. The free bases isolated from the hydrochlorides were then distilled; here the low-boiling amines were trapped as the hydrochlorides. Under our conditions for the case of acrylonitrile we isolated γ-butoxypropylamine in a 59.6% yield, and propylamine in an 11% yield.

The reduction of metacrylonitrile also gave two amines. Of them one proved to be isobutylamine, and the other, on the basis of its properties and analysis, was assigned the structure of γ-butoxyisobutylamine (I). Here the amount of isobutylamine that was obtained slightly exceeded the amount of formed alkoxyamine.



(I)

We also obtained two substances in the reduction of allyl cyanide, which under the reaction conditions isomerized into crotononitrile (so that actually we were dealing with the latter). The low-boiling product from the reaction was butylamine, while the higher-boiling fraction was γ-butoxybutylamine (II). The latter was obtained



(II)

in nearly twice the amount of the butylamine. The total yield here proved to be lower than for the reduction of acrylonitrile and metacrylonitrile, and specifically it was about 63%, while for the mentioned compounds we obtained yields of 71 and 81%, respectively.

We found only one base in the reduction products of β,β-dimethylacrylonitrile, proving to be isoamylamine. Consequently, the alcohol failed to add to this nitrile under our conditions.

In the case of the 1-cyclohexenecarboxonitrile we, the same as Ruzicka [4], found that the reduction leads to the formation of only one amine, and specifically – to (aminomethyl) cyclohexane.

The reduction of cinnamonitrile under our conditions also gave only one reaction product, namely γ-phenylpropylamine.

In the last three cases the yields of the amines was of the order of 50-60%. All of the results obtained by us are summarized in Table 1.

As the above-presented experiments show, in the general case for the reduction of α,β-unsaturated nitriles by the Vyshnegrad method the following reactions can take place:

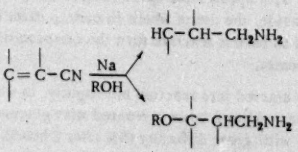


TABLE 1

Reduction of α,β-unsaturated nitriles with sodium in n-butyl alcohol

Starting nitrile	Reaction products	Yield (in %)	Total yield (in %)	Ratio of alkoxy-amine to alkyl-amine (in moles)
$CH_2=CH-CN$	$CH_3CH_2CH_2NH_2$ $C_4H_9O(CH_2)_3NH_2$	11.0 59.6	70.6	5.5 : 1
$CH_2=CHCH_2CN$ $CH_3CH=CHCN$	$CH_3(CH_2)_3NH_2$ $C_4H_9OCH(CH_3)CH_2CH_2NH_2$	23.7 39.6	63.3	1.7 : 1
$CH_2=CCN$ $\quad\quad\vert$ $\quad\quad CH_3$	$CH_3CH(CH_3)CH_2NH_2$ $C_4H_9OCH_2CH(CH_3)CH_2NH_2$	46.2 34.6	80.8	1 : 1.3
		60.5		—
		50.3		—
$C_6H_5CH=CHCN$*	$C_6H_4(CH_3)_2NH_2$	56.4		—

* There is a brief statement [5] that γ-phenylpropylamine is formed in the reduction of cinnamonitrile.

The first stage, undoubtedly, is addition at the double bond, and not hydrogenation of the nitrile group. All of the nitriles taken by us add hydrogen, both at the carbon-carbon double bond and at the nitrile group. In a number of cases (acrylonitrile, crotononitrile, methacrylonitrile) the alcohol addition reaction proceeded concurrently with the addition of hydrogen at the double bond, and here together with the amines, corresponding to the starting nitriles, we obtained alkoxyamines.

As a result, we were able to establish that under our conditions the addition of alcohols proceeds only with those α,β-unsaturated nitriles where there is either none or only one alkyl radical at the double bond. On the other hand, the presence of substituents, apparently, facilitates hydrogen addition to the double bond.

EXPERIMENTAL

Crotononitrile was obtained by the isomerization of allyl cyanide, b.p. 111-115.5° at 758 mm, n_D^{20} 1.4230. The mixture contains approximately equal amounts of the cis- and trans- forms. Literature [6] for the cis- form: b.p. 107.4° at 757 mm, n_D^{20} 1.42065; for the trans- form: b.p. 122.05° at 757 mm, n_D^{20} 1.42480.

β,β-Dimethylacrylonitrile [7]. A mixture of 20.9 g of methallyl chloride and 23.1 g of copper cyanide in nitrobenzene solution was heated in an oil bath at 125-130° for 5 hours under reflux. After removal of the unreacted chloride the methallyl cyanide was distilled. B.p. 135-137.5° at 767 mm, n_D^{20} 1.4200. Yield 9.9 g(62.4%). The methallyl cyanide was isomerized in a manner similar to the isomerization of allyl cyanide. Yield 42.2%, b.p. 139-141° at 762 mm. Literature: b.p. 140-142° at 760 mm [7].

Methacrylonitrile was obtained by the dehydration of acetone cyanohydrin. In a liter distilling flask fitted with a short outlet tube 40 g of freshly distilled acetone cyanohydrin was thoroughly mixed with 100 g of phosphorus pentoxide; here strong self-heating was observed. The mixture was cautiously heated with a free flame until liquid failed to distill. The distillate was distilled from a Favorsky flask and fractionated twice. The yield of methacrylonitrile was 13.2 g (41.9%), b.p. 87-90° at 752 mm (most of the nitrile distilled at 89-90°), n_D^{20} 1.4022. Literature: b.p. 88-91°, n_D^{20} 1.3999 [8].

1-Cyclohexenecarboxonitrile was obtained by the pyrolysis of cyclohexanone cyanohydrin acetate [9]. The acetate (b.p. 100-102° at 1-1.5 mm) in a stream of nitrogen was passed through a tube filled with glass wool. The furnace temperature was maintained at 450-500°. The passage rate was 10-15 drops per minute. The catalyzate was treated with soda solution, dried over sodium sulfate, and fractionally distilled in vacuo. Three fractions were collected: 1st fraction, b.p. to 69.5° (10 mm); 2nd fraction, b.p. 69.5-74° (10 mm); 3rd fraction, b.p. 100°

(3 mm) and higher. The pure nitrile was isolated from the 2nd fraction by distillation, b.p. 71-72° at 10 mm, n_D^{20} 1.4826. The total yield of the nitrile from 45 g of the acetate was 19.2 g (64.6%). According to [9]: b.p. 78-80° at 12 mm.

Cyclohexylideneacetonitrile was obtained by reacting cyclohexanone with cyanacetic acid in pyridine [7], yield 60.3%, b.p. 103.5-105° at 20 mm, n_D^{20} 1.4812. According to [7]: b.p. 105-110° at 21 mm, n_D^{20} 1.4824.

Cinnamonitrile [10] was prepared from benzaldehyde and cyanacetic acid in the presence of pyridine in 42.7% yield. B. p. 125-130° at 12 mm, n_D^{20} 1.5942. (The nitrile consisted for the most part of the trans- form). Literature [10]: trans- form, b.p. 128.8° at 12 mm, n_D^{20} 1.60324; cis- form, b.p. 115.2° at 12 mm, n_D^{20} 1.58488.

Reaction with Glycine [1]. Into a 50-ml conical flask with ground-glass stopper was pipetted 10 ml of a 0.5 M aqueous potassium glycinate solution (containing 38 g of glycine and 28 g of potassium hydroxide in 1 liter of solution) and to it was added the weighed nitrile sample (about 0.002 mole). The flask was stoppered tightly and shaken on a mechanical rocker at room temperature for either 1 or 2 hours, after which the solution was neutralized with acetic acid (8-10 drops of glacial acid) to phenolphthalein. (The neutralized solution can stand indefinitely without change). Then 2 ml of 50% potassium iodide • solution was added and the solution was made up with water to 200 ml in a volumetric flask. One ml of this solution was taken for the gasometric determination of amino nitrogen in the Ioanisiani apparatus. The diazotization was run for 3 minutes.

The yield from the reaction of the nitrile with glycine was determined by the equation:

$$\text{Percent addition} = \frac{10 \cdot M}{14 \cdot S}(T - 2a), \tag{1}$$

where M is the molecular weight of the nitrile, S is the weight of nitrile, a is the number of milligrams of nitrogen in 1 ml of the solution, found by the gasometric method, and T = T'/10 (where T' is the number of milligrams of nitrogen in 1 ml of the glycinate solution).

T' was determined in a separate experiment, where a weighed sample of acrylonitrile was taken;•• T was found from the equation:

$$T = \frac{140 \cdot S'}{M'} + a', \tag{2}$$

where M' is the molecular weight of acrylonitrile, S' is the weight of acrylonitrile, and a' is the number of milligrams of nitrogen in 1 ml of the solution, found by the gasometric method.

If we set M' = 53.06, we obtain instead of equation (2) the simpler expression:

$$T = \frac{S'}{0.379} + a'. \tag{3}$$

All of the determination results are summarized in Table 2.

Reduction of α,β-Unsaturated Nitriles

Acrylonitrile. To 15 g of metallic sodium, melted in 30 ml of toluene, from a dropping funnel over 15 minutes was added a solution of 3.2 g of acrylonitrile in 220 ml of anhydrous n-butyl alcohol. On conclusion of reaction the alcoholate was decomposed with water (200 ml) and the mixture was steam-distilled. The distillate was collected in dilute hydrochloric acid. The alcohol layer was separated and steam-distilled so as to separate the base from the alcohol and toluene. The residue from the distillation was combined with the acid from the Tishchenko flask, which was connected to the reflux condenser, and also with the water layer of the distillate from the first distillation, and evaporated on the water bath. The hydrochloride (viscous oil) was placed in a thick-walled flask, fitted with a reflux condenser, decomposed with powderlike sodium hydroxide, and repeatedly extracted with ether. The ether solution (about 400 ml) was dried over potassium hydroxide, the ether distilled into a receiver containing hydrochloric acid, and the residue vacuum-distilled. As a result there was

• The KI is necessary in order to obtain constant analysis results for the glycine.

•• Here a 100-ml volumetric flask was used.

isolated 0.62 g (11.0%) of propylamine hydrochloride and 4.67 g (59.6%) of γ-butoxypropylamine with b.p. 71.5-72.5° at 19 mm.

TABLE 2

Nitriles	Time (in hours)	Weight (in g)	a	Percent addition
Acrylonitrile	1	0.1250	0.372*	100
Crotonitrile	1	0.1385	0.330	14.5
	2	0.1390	0.318	22.7
Allyl cyanide	1	0.1403	0.347	2.7
	2	0.1325	0.344	5.3
Methacrylonitrile	1	0.1355	0.348	1.7
	2	0.1332	0.344	5.0
1-Cyclohexenecarboxonitrile	1	0.2209	0.346	3.5
	2	0.2036	0.341	7.5
Cyclohexylideneacetonitrile	1	0.2356	0.346	3.7
	2	0.2492	0.340	7.6
Cinnamonitrile	1	0.2586	0.349	1.4
	2	0.2561	0.345	4.3

* From which T = 0.702.

Methacrylonitrile. The reduction was run the same as before. For 8 g of methacrylonitrile there was taken 26.5 g of metallic sodium and 420 ml of the alcohol. When the reaction products were distilled the 1st fraction (up to 83° at 25 mm) was returned to the ether distillate. γ-Butoxyisobutylamine was isolated from the main 2nd fraction; yield 5.98 g (34.6%).

B.p. 83-85° at 25 mm, n_D^{20} 1.4270, d_4^{20} 0.8412, MR_D 44.33; calc. 44.19.

Found %: C 66.32; 66.39; H 13.33, 13.35. $C_8H_{19}ON$. Calculated %: C 66.16; H 13.19.

γ-Butoxyisobutylamine Picrate, m.p. 63° (from benzene).

The distilled ether was acidified with hydrochloric acid. The white flocculent precipitate obtained after removal of the ether was treated with anhydrous ethyl alcohol. There was isolated 6.02 g of isobutylamine hydrochloride with m.p. 178-179°, which agrees with the literature. The yield was 46.2%, based on starting methacrylonitrile.

Allyl Cyanide (Crotononitrile). The reaction was run with 6.4 g of allyl cyanide, 22 g of sodium and 350 ml of the alcohol. With the usual treatment there was isolated from the ether distillate and lower-boiling fraction 2.42 g (23.7%) of butylamine as the hydrochloride. After precipitation from alcohol with ether the m.p. was 196-197°, which agrees with the literature. After two distillations the higher-boiling fraction gave γ-butoxybutylamine with b.p. 78-79° at 19 mm. Yield 5.39 g (39.6%, based on taken allyl cyanide).

n_D^{20} 1.4308, d_4^{20} 0.8442, MR_D 44.51; calc. 44.19.

Found %: C 66.52, 66.30; H 13.35, 13.31. $C_8H_{19}ON$. Calculated %: C 66.16; H 13.19.

Picrate, m.p. 112° (from benzene).

1-Cyclohexenecarboxonitrile. For the reduction of 8.04 g of the nitrile there was taken 17.5 g of metallic sodium and 280 ml of the alcohol. Evaporation of the acid distillate obtained after steam distillation gave a solid hydrochloride with m.p. about 210°. After treatment with alkali and ether there was obtained 4.26 g (50.3%) of (aminomethyl) cyclohexane with b.p. 79-80° at 50 mm.

Picrate, m.p. 186-187°. Literature: b.p. 56-58° at 12 mm [4]; picrate, m.p. 184-186° [11].

β,β-Dimethylacrylonitrile. The reduction was run with 6.9 g of the nitrile and 19.5 g of sodium in

310 ml of the alcohol. Decomposition of the hydrochloride gave isoamylamine. Yield 4.42 g (60.5%). B.p. 92-95° at 748 mm, which agrees with the literature.

Cinnamonitrile. The reduction was run in similar manner. To 17.5 g of metallic sodium was added a solution of 9.67 g of the nitrile in 280 ml of the alcohol. Treatment of the hydrochloride with solid caustic yielded only one base. Two distillations in vacuo gave 5.74 g of γ-phenylpropylamine (56.4%) with b.p. 116-118° at 20 mm.

Picrate, m.p. 153.5-154° (from alcohol). Literature: b.p. 112-114° at 18 mm [12]; picrate, m.p. 152° [5].

SUMMARY

1. The comparative tendency shown by α,β-unsaturated nitriles for addition was studied on the example of reacting glycine with the nitriles: acrylonitrile, crotononitrile, methacrylonitrile, β,β-dimethylacrylonitrile, cyclohexylideneacetonitrile, 1-cyclohexenecarboxonitrile and cinnamonitrile. The first two nitriles proved to be the most active.

2. When these nitriles were reduced with sodium in n-butyl alcohol it was revealed for acrylonitrile, crotononitrile and methacrylonitrile that, together with the usual reduction products, γ-butoxyalkylamines are formed, whereas the remaining nitriles give only the corresponding saturated amines.

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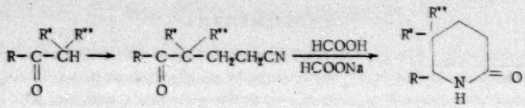
REDUCTION OF FORMIC ACID AND ITS DERIVATIVES

III. SYNTHESIS OF SUBSTITUTED α-PIPERIDONES

A. N. Kost, T. A. Shchegoleva and L. G. Yudin

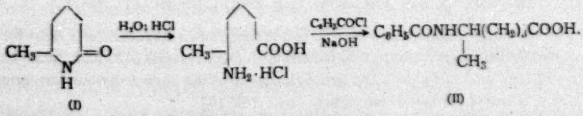
2-Phenyl-6-piperidone is formed when methyl γ-benzoylbutyrate is heated with formamide [1]. Lukes and Sorm [2], and later Lukes and Vecera [3], studied the reaction of formamide with γ- and δ-keto acids, and described the synthesis of a number of α-piperidones and α-pyrrolidones. They [3] found that the dihydropyridones and hydroxypiperidones are reduced by formic acid to α-piperidones. Together with this, the amides of δ-keto acids easily lose water when heated, being transformed into dihydropyridones [4].

We obtained a number of α-piperidones by reacting δ-keto nitriles with formic acid and sodium formate.



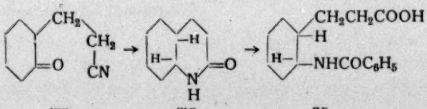
The starting keto nitriles were obtained by the action of acrylonitrile on ketones. In the process the accumulations of starting substances were changed and the earlier described cyanoethylation methods were improved.

The reduction of γ-acetobutyronitrile gave the earlier described [5] 2-methyl-6-piperidone (I) (in 68% yield), which on hydrolysis with subsequent benzoylation gave δ-benzoylaminocaproic acid (II) [5]:



(I) (II)

In the same way γ-acetylvaleronitrile (in 74 % yield) was converted into 2,3-dimethyl-6-piperidone. Some difficulties arose in isolating the 2-methyl-3-ethyl-6-piperidone, which was obtained in crystalline form only after vacuum-distillation. The reduction of γ-methyl-γ-isobutyrylvaleronitrile gave 3,3-dimethyl-6-piperidone (in 56% yield), which on hydrolysis with hydrochloric acid gave the difficultly crystallizing hydrochloride of 5-amino-4,4,6-trimethylheptanoic acid. Attempts to benzoylate this compound proved unsuccessful, since on the slightest alkalization it immediately was converted into the starting lactam. The reduction of 2-(2'-cyanoethyl)cyclohexanone (III) gave in 72% yield the trans-octahydro-α-quinolone (IV) (i.e. octahydrocarbostyryl), identified by its conversion into trans-(2-benzoylaminocyclohexyl)propionic acid (V) [6]:



(III) (IV) (V)

The cis- form of the octahydrocarbostyryl was not found, which is evidence of the stereo specificity of the reaction. 2,3-Dimethyl-6-piperidone was also isolated in only one of its stereo forms; however, its configuration was not investigated.

Having obtained entirely satisfactory results in the reduction of δ-keto nitriles, we attempted to reduce a γ-keto nitrile, and specifically β-benzoylpropionitrile. Here it was found that tar-formation results when the compound is heated with formic acid (possibly, due to the intermediate formation of the pyrrole compound). Together with this, the corresponding amide (β-benzoylpropioamide) gave 2-phenyl-5-pyrrolidone in 32 % yield, which was identified by its hydrolysis to γ-amino-γ-phenylbutyric acid. With formamide β-benzoylpropionitrile forms a red-brown dye, postulated as having the structure bis-(2-phenyl-5-pyrrole)azamethine. The formation of this type of substance was observed earlier by Davies and Rogers [7] in the reaction of formamide with α-phenyl-β-benzoylpropionitrile.

As a result, the reaction with γ-keto nitriles proceeds differently than with the corresponding amides or acids. This permits postulating that the process for the formation of lactams fails to go through the keto acid stage (and later by the scheme of the Leuckart reaction). Apparently, here cyclization takes place first, and then reduction of the cyclic nitrogen compound.

EXPERIMENTAL

2-Methyl-6-piperidone (I). The addition (in 2.5 hours) of 53 g of acrylonitrile to 260 g of acetoacetic ester in the presence of sodium ethylate (0.4 g of sodium in 10 ml of anhydrous alcohol) with subsequent standing for 48 hours at room temperature gave 98 g (50%) of γ-carbethoxy-δ-oxocapronitrile, b.p. 143-144° at 8 mm, n_D^{20} 1.4462 (a yield of 23% was indicated earlier [8]). The boiling of 90 g of γ-carbethoxy-δ-oxocapronitrile and 90 g of potash in 800 ml of water (for 3.5 hours), after ether extraction and distillation, gave 37.7 g (70%) of δ-oxocapronitrile, • b.p. 108-109° at 12 mm, n_D^{20} 1.4403, which agrees with the literature [9, 10].

A mixture of 10 g of δ-oxocapronitrile, 34 g of sodium formate and 23 g of anhydrous formic acid was heated for 62 hours under reflux. The reaction mixture was diluted with water to dissolve the sodium formate and then under cooling was made strongly alkaline with 40% sodium hydroxide solution. The precipitate obtained here was filtered, washed with water and dried in a desiccator. Yield 6.85 g (68%). After recrystallization from ether the 2-methyl-6-piperidone had m.p. 85°. Literature: m.p. 84° [5], 84-85° [11], 85-86.5° [1], 87-88° [12].

The boiling of 5 g of 2-methyl-6-piperidone with 30 ml of concentrated hydrochloric acid for 5 hours gave after evaporation an oil that failed to crystallize (it is indicated in the literature [12] that the hydrochloride of δ-aminocaproic acid crystallizes with difficulty), the benzoylation of which gave δ-benzoylaminocaproic acid (II) with m.p. 146-147° (from aqueous alcohol). Literature: m.p. 148° [5].

2,3-Dimethyl-6-piperidone. The treatment of 178 g of methyl ethyl ketone with 26.5 g of acrylonitrile (at room temperature for 24 hours) in the presence of sodium ethylate (0.3 g of sodium in 10 ml of anhydrous alcohol) gave 17.4-18.7 g (27-30 %) of γ-acetylvaleronitrile, •• b.p. 110-111° at 12 mm, n_D^{20} 1.4355, which data agree with the literature [13-15].

• If soda solution is used for the cleavage of the γ-carbethoxy-δ-oxocapronitrile (40 g of soda, 360 ml of water and 40 g of the nitrile), then the yield of δ-oxocapronitrile drops to 59%.

•• The reaction mixture had to be neutralized (best of all with acetic acid) before it could be distilled. The starting ketone should be very pure. The technical product, when aqueous or alcoholic potassium hydroxide or sodium hydroxide solutions, sodium ethylate or the Rodionov catalyst (an alcohol solution of ethoxytrimethylphenylammonium) are used as catalysts, gives yields that fail to exceed 8%. When large amounts of alkaline agents are introduced into the reaction the acrylonitrile begins to polymerize and the formation of the dicyanoethylated product predominates. The methyl ethyl ketone used by us was dried over potash and distilled through a 30-theoretical plate column (b.p. 79.4-79.6° at 752 mm). The use of a 10-fold excess of the ketone [14] fails to raise the yield.

A mixture of 10 g of γ-acetylvaleronitrile, 30.5 g of sodium formate and 20.8 g of anhydrous formic acid was heated for 30 hours under reflux, and then another 12.2 g (10 ml) of anhydrous formic acid was added and the heating continued for another 30 hours. Having diluted the reaction mixture with water to completely dissolve the precipitate, the solution was then made strongly alkaline (under cooling) with 40% aqueous sodium hydroxide solution. The precipitate obtained here was filtered, washed with water and dried in a desiccator. The yield of 2,3-dimethyl-6-piperidone was 7.4 g (74%). After recrystallization from gasoline it had m.p.98-99°. Subsequent recrystallizations from ether or isoctane gave a m.p. of 99°.

Found %: N 11.12, 11.21. $C_7H_{13}ON$. Calculated %: N 11.01.

γ-Acetylcapronitrile. * a) To 109 g of dried potash and twice-distilled methyl propyl ketone (b.p. 101.5-102° at 756 mm) was added 3 ml of 10% sodium ethylate solution in alcohol and with constant stirring 17.1 g of acrylonitrile was added dropwise at room temperature in 1.5 hours (the reaction mixture showed slight self-heating and turned yellow). Then, without ceasing to stir, the mixture was heated another 6 hours on the water bath (the bath temperature was 40-50°), neutralized under stirring with glacial acetic acid, the unreacted starting substances distilled off in one hour, and the residue vacuum-distilled, collecting the fraction with b.p. 115-116° at 5 mm. The yield of γ-acetylcapronitrile was 11.6 g (26%).

n_D^{20} 1.4381, d_4^{20} 0.9624, MR_D 37.98; calc. 38.24. Literature: b.p. 67° at 0.2 mm [16], 90-93° at 3 mm [17]; 109-110° at 7.5 mm [13], n_D^{25} 1.4365 [16].

b) To a mixture of 30 g of ethyl α-ethylacetoacetate (b.p. 78-79° at 10 mm, n_D^{20} 1.4229, d_4^{20} 0.9808) and 4 ml of 10% sodium ethylate solution in alcohol with stirring and at 10-12° was added dropwise in 15 minutes 10 g of acrylonitrile and stirring was continued for another 4 hours at 15-20° (or at 10-15°). After acidification with acetic acid the alcohol, acetic acid and starting substances were distilled off under slight vacuum, and the residue was vacuum-distilled. The yield of γ-acetyl-γ-carbethoxycapronitrile was 28.4-28.6 g (71-71.5%).

B.p. 164-164.5° at 11 mm, n_D^{20} 1.4502, d_4^{20} 1.0518, MR_D 54.21; calc. 54.42.

Found %: N 6.54, 6.76. $C_{11}H_{17}O_2N$. Calculated %: N 6.63.

A mixture of 25 g of γ-acetyl-γ-carbethoxycapronitrile, 350 ml of water and 32 g of soda was boiled under reflux for 4 hours. The reaction product was salted out with potash, the oil layer separated, the water layer extracted four times with ether, the ether extracts added to the main product, the combined mixture acidified with sulfuric acid, and then dried over sodium sulfate. After removing the ether the residue was vacuum-distilled. The yield of γ-acetylcapronitrile was 4.0 g (21%), b.p. 142-143° at 28 mm, n_D^{20} 1.4378, d_4^{20} 0.9621. If boiling for 10 hours with potash solution is used for the cleavage, then the yield drops to 11%.

2-Methyl-3-ethyl-6-piperidone. A mixture of 11.0 g of γ-acetylpropionitrile, 18.4 g of anhydrous formic acid and 27.1 g of sodium formate was heated for 40 hours under reflux, after which another 12.2 g (10 ml) of anhydrous formic acid was added and the heating was continued for another 23 hours. The mixture, after dilution with water, was made alkaline, the oil obtained here was extracted with ether, the extract dried over magnesium sulfate, the ether distilled off, and the residue vacuum-distilled. The yield of 2-methyl-3-ethyl-6-piperidone was 5.3 g (i. e. 50%), b.p. 152-155° at 14 mm, m.p. 40-43° (from isopentane).

Found %: N 9.97, 10.16. $C_8H_{15}ON$. Calculated %: N 9.92.

3,3-Dimethyl-2-isopropyl-6-piperidone. A mixture of 10 g of γ-methyl-γ-isobutyrylvaleronitrile [18], 13.8 g of anhydrous formic acid and 20.4 g of sodium formate was heated for 40 hours under reflux, after which another 10 ml (12.2 g) of formic acid was added and the mixture heated another 20 hours. After diluting the mixture with water (to dissolve the sodium formate) the oil layer was separated, which crystallized on cooling. The mixture was made alkaline, which increased the amount of precipitate, and the precipitate was filtered and washed with water. There was obtained 5.6 g of 3,3-dimethyl-2-isopropyl-6-piperidone. Yield 56%. After recrystallization from gasoline, and then from isoctane, the substance melts at 111-112°.

Found %: C 70.68, 70.73; H 11.20, 11.28; N 8.18, 8.36. $C_{10}H_{19}ON$. Calculated %: C 70.98; H 11.32; N 8.27.

Trans-Octahydro-α-quinolone (IV). A mixture of 10 g of 2-(2'-cyanoethyl)cyclohexanone [10, 14, 19], 16.1 g of anhydrous formic acid and 23.8 g of sodium formate was heated for 20 hours under reflux (the reaction

* The experiments were run by V. V. Rode.

is not complete if the heating is only for 10 hours, while heating for 60 hours fails to increase the yield). Dilution of the mixture with water gave an upper viscous oily layer. When the cooled reaction mass was made alkaline the oil layer gradually formed crystals, which settled to the bottom. Separation of the crystals, washing them with water and drying in a desiccator, gave 7.2 g of trans-octahydro-α-quinolone (72% yield) with m.p. 149-150°. After 2 recrystallizations from alcohol, and then from water, m.p. 151°. Literature: m.p. 151° [6], 152-153° [20].

When 2-(2'-cyanoethyl) cyclohexanone was boiled (5 hours) with a 10-fold amount of anhydrous formic acid in the presence of skeletal nickel the octahydro-α-quinolone could not be isolated.

A mixture of 1.0 g of octahydro-α-quinolone and 10 ml of concentrated hydrochloric acid was boiled under reflux for 5 hours, and then evaporated on the water bath. On standing in a vacuum-desiccator the oily residue crystallized. There was obtained 0.7 g of β-(2'-aminocyclohexyl) propionic acid hydrochloride, m.p. 173-174° (when precipitated from anhydrous alcohol with anhydrous ether). The benzoylation of this hydrochloride in aqueous-alkali medium gave the trans-β-(2'-benzoylaminocyclohexyl) propionic acid (V) with m.p. 200° (from alcohol). Literature: m.p. 200° [6,20].

β-Benzoylpropioamide. To a mixture of 10.0 g of β-benzoylpropionitrile, obtained by the action of sodium cyanide on β-dimethylaminopropiophenone hydrochloride [21], 200 ml of 3% hydrogen peroxide solution and 2 ml of 6N sodium hydroxide solution was added ethyl alcohol until the mixture was homogeneous (about 40 ml); then the solution was heated with constant stirring for 5 hours at 50-60°. The cooled solution was neutralized with 2N sulfuric acid, evaporated to 1/5 of its original volume, and the precipitate obtained here was recrystallized twice from alcohol. The yield of pure β-benzoylpropioamide was 5.0 g (45%), m.p. 125°. Literature: m.p. 125° [22].

A solution of 9.0 g of β-benzoylpropionitrile in 30 ml of concentrated sulfuric acid was prepared. After 2 hours the mixture was poured over ice. The precipitate obtained here was recrystallized twice from alcohol. The yield of β-benzoyl-propioamide with m.p. 125° was 3.0 g (30%).

2-Phenyl-5-pyrrolidone. A mixture of 5.0 g of β-benzoylpropioamide, 10.2 g of sodium formate and 7.0 g of anhydrous formic acid was boiled under reflux for 40 hours, and water added after cooling to dissolve the sodium formate. The tar was filtered; the solution made alkaline with 40% sodium hydroxide. Precipitate obtained was vacuum dried. Heating the tarry residue for 5-10 minutes on the water bath with hydrochloric acid (1:1) permitted extracting a little more substance, which precipitated when the acid extract was made alkaline with caustic. The total yield of 2-phenyl-5-pyrrolidone was ~ 1.5 g (30%). After 2 recrystallizations from benzene, m.p. 108°. Literature: m.p. 110° [23].

The boiling of 0.8 g of 2-phenyl-5-pyrrolidone for 10 hours with 10 ml of concentrated hydrochloric acid, followed by evaporation to dryness, gave 1 g of crystalline γ-amino-γ-phenyl-butyric acid hydrochloride, which after 2 recrystallizations from alcohol melts at 179°. Literature: m.p. 180° [23].

If a mixture of 8 g of β-benzoylpropionitrile with 12 g of anhydrous formic acid and 13.6 g of sodium formate is boiled, then immediately strong tarring is observed. A tarry mass is obtained after boiling for 26 hours, from which we were able to isolate a minute amount of 2-phenyl-5-pyrrolidone with m.p. 107-108° (from benzene).

The heating of β-benzoylpropionitrile with formamide (containing about 8% of ammonium formate) for 6 hours at 150-160°, after pouring into water, gave a brownish-red substance, which decomposed when heated to 250°, and which was found to be readily soluble in ether, alcohol and benzene.

SUMMARY

1. A new synthesis of α-piperidones by the reduction of δ-keto nitriles with a mixture of formic acid and sodium formate was described.

2. The stereo specificity of this reaction was demonstrated on the example of synthesizing octahydro-α-quinolone.

3. The action of formic acid in admixture with sodium formate on β-benzoylpropioamide gave 2-phenyl-5-pyrrolidone.

4. Improved methods for the synthesis of a number of δ-keto amides were given (proceeding from the ketones and acrylonitrile.

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THE REACTION OF α-AND β-CHLORO ALKYLSILANE CHLORIDES WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE

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In the alkyl halide series (C–Cl bond) the Friedel-Crafts reaction has been studied on thousands of examples. However, in the silane halide series (Si–Cl bond), being structurally similar to the corresponding carbon analogs, this reaction has hardly been studied. Such a situation is explained by the fact that under the usual conditions it is impossible to silicoalkylate with the aid of $R_{4-n}SiX_n$, not only because the affinity of the electropositive silicon toward the electronegative halogen is greater than it is toward the aryl (or alkyl) radical, but also for the possible reason that the $Si-C_{aryl}$ bond, formed in the reaction, is immediately decomposed by the aluminum chloride.

For the chloroalkylsilane chlorides, i.e. for compounds that have a halogen atom at both the carbon and silicon atoms, the Friedel-Crafts reaction is realized quite easily even under the usual conditions; however, here the reaction proceeds exclusively at the C–Cl bond, the Si–Cl bond being left completely alone. However, it is only recently that the chloroalkylsilane chlorides, a convenient method having been worked out for their synthesis, have become available compounds [1, 2], and a study of these interesting reactions also still finds itself in the initial stages and limited to only a few investigations, as follows: some patent data [3-7], the communications of Wagner and coworkers [8], and the present studies, the preliminary communication of which was recently published [2].

We studied the silicoalkylation of aromatic compounds with different α- and β-chloroalkyltrichlorosilanes. It was found that the reaction with primary α-chlorides proceeds with great difficulty, and requires heating at 80-100° for a long time, in which connection about 60% of the chloride is recovered unchanged. On going to a secondary α-chloride (α-chloroethyltrichlorosilane) the reaction proceeds with somewhat greater vigor, and the amount of chloride entering into reaction rises to 70-80%. Dichloromethyltrichlorosilane $Cl_2CHSiCl_3$, when using a small amount of $AlCl_3$ (0.2 mole for 1 mole of the chloride), failed to react with benzene. However, it did react when the amount of $AlCl_3$ was increased 3-fold. The reaction was run for 54 hours and gave trichlorosilyldiphenylmethane in ~10% yield. Bis(trichlorosilyl)chloromethane $Cl_3SiCHClSiCl_3$ proved to be completely unreactive – in this case reaction failed to be observed even when an excess of $AlCl_3$ was used with prolonged heating at 150°.

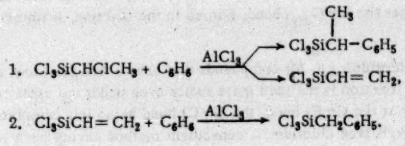
When compared to the α-chlorides the β-chlorides possess higher activity. The reaction with the β-chloroethyltrichlorosilane begins even at room temperature and is ended in 20-30 hours; at elevated temperature (80-100°) the reaction proceeds in several hours. The β-chloride reacts completely in all cases, in which connection the yields of reaction products (with benzene, toluene and chlorobenzene) are 70-80%. The (β-chloroethyl)ethyldichlorosilane is characterized by even greater activity. A violent reaction began immediately after the addition of the first drops of the chloride solution in benzene to a mixture of benzene and $AlCl_3$, and the temperature of the mixture quickly rose to 40-50°. The reaction was ended in 5-8 hours after all of the chloride had been added.

As a result, the activity of the investigated chloroalkylsilane chlorides in the Friedel-Crafts reaction can be arranged in the following order:

$$C_2H_5SiCl_2CH_2CH_2Cl > Cl_3SiCH_2CH_2Cl > Cl_3SiCHClCH_3 >$$
$$> Cl_3SiCH_2Cl > Cl_3SiCHCl_2 > Cl_3SiCHClSiCl_3.$$

As the result of reacting α-chloroethyltrichlorosilane with benzene there was isolated, together with α-phenylethyltrichlorosilane, also the β-phenylethyltrichlorosilane. The ratio of the α-isomer to the β-isomer was ~2.3:2. That the β-isomer is formed in this reaction was also observed by Wagner and coworkers [8]. To elucidate the mechanism of this process we studied the reaction of $AlCl_3$ with the α- and β-chloroethyltrichlorosilanes separately. As communicated earlier by Wagner and coworkers, the heating of (β-chloroethyl)-trichlorosilane with $AlCl_3$ gives vinyltrichlorosilane in ~50% yield, based on the amount of chloride taken for reaction, and 70%, based on reacted chloride. This reaction was repeated by us and it was shown that if additional $AlCl_3$ is introduced, after about half of the theoretical amount of vinyltrichlorosilane has been distilled off, that the chloride can be made to react completely and give the same yield of vinyltrichlorosilane (70%). We were the first to study the reaction of (α-chloroethyl)trichlorosilane with aluminum chloride. It was found that in this case also the vinyltrichlorosilane is formed in ~50% yield, based on starting α-chloride. A considerable amount of silicon tetrachloride is formed along with the vinyltrichlorosilane. As a result, in the alkylation of both the α- and β-chloroethyltrichlorosilanes, vinyltrichlorosilane is present in the reaction mixture.

As was shown by Wagner and coworkers [8], the silicoalkylation of benzene with vinyltrichlorosilane leads only to (β-phenylethyl)trichlorosilane (the addition of HCl to $CH_2=CHSiCl_3$ proceeds exclusively against the Markovnikov rule). As a result, the scheme for the formation of the β-isomer in the silicoalkylation with the α-chloride can be depicted by the following reactions:



1. $Cl_3SiCHClCH_3 + C_6H_6 \xrightarrow{AlCl_3} Cl_3SiCH(CH_3)-C_6H_5 + Cl_3SiCH=CH_2$,

2. $Cl_3SiCH=CH_2 + C_6H_6 \xrightarrow{AlCl_3} Cl_3SiCH_2C_6H_5$.

However, it is impossible to exclude the possibility of α-chloride isomerization into the β-chloride under the influence of $AlCl_3$.

All of the silane chlorides obtained by silicoalkylation were methylated with CH_3MgI and the corresponding trimethylsilanes were obtained. To determine the position of the chlorine and methyl in the silicoalkylation products of chlorobenzene and toluene the β-(chlorophenyl)ethyltrimethylsilane and β-tolylethyltrimethylsilane were oxidized. The product isolated in the first case was p-chlorobenzoic acid, and consequently, the silicoalkylation product of chlorobenzene is, apparently, mainly the para-isomer. Terephthalic acid was isolated in the second case, i.e. the silicoalkylation product of toluene also appears to be essentially the para-isomer.

EXPERIMENTAL

1. Benzyltrichlorosilane. A mixture of 60 g of chloromethyltrichlorosilane, 8.5 g of $AlCl_3$ and 95 g of benzene was charged into a flask, fitted with stirrer, thermometer and reflux condenser. The reaction mixture was heated at the boil (80-95°) under vigorous stirring for 80-100 hours until the evolution of HCl ceased. To remove the $AlCl_3$ the mixture was treated with 0.06 mole of $POCl_3$ and 100 ml of heptane. After heating for 30 minutes, followed by cooling, the precipitate was filtered and the filtrate was distilled. There was isolated 41.8 g of chloromethyltrichlorosilane (b.p. 116-117.5°) and 13.8 g of benzyltrichlorosilane, or a yield of 62% (based on reacted α-chloride), b.p. 213-214° (756 mm), n_D^{20} 1.5252, d_4^{20} 1.2796, MR_D 54.00; calc. 53.41.

The obtained benzyltrichlorosilane was fully methylated. To the Grignard reagent, prepared from 3.5 g of Mg and 18.5 g of methyl iodide, was added 10 g of $C_6H_5CH_2SiCl_3$. After suitable treatment and distillation there was obtained 5.8 g (80%) of trimethylbenzylsilane with b.p. 191-192° (748 mm), n_D^{20} 1.5042, d_4^{20} 0.8933, MR_D 54.38; calc. 54.52.

Found %: C 73.34, 73.42; H 9.82, 9.83; Si 16.95, 16.84. $C_{10}H_{16}Si$. Calc. %: C 73.17; H 9.76; Si 17.07

2. p-Chlorophenylmethyltrichlorosilane. The reaction was run in the above-described apparatus. For reaction there was taken 120 g of chloromethyltrichlorosilane, 336 g of chlorobenzene and 42 g of aluminum chloride. Stirring was maintained for 80 hours at 120-140°. Then, the same as in Experiment 1, the aluminum chloride was removed. Distillation gave 120 g of chloromethyltrichlorosilane with b.p. 115-117° (745 mm)

and 22.0 g of (p-chlorophenyl)methyltrichlorosilane, or a yield of 45%, based on reacted α-chloride, b.p. 103-104° (100 mm), n_D^{20} 1.5395, d_4^{20} 1.3606, MR_D 59.65; calc. 58.28.

For methylation 12.5 g of $Cl_3SiCH_2C_6H_4Cl$ and 0.2 mole of the Grignard reagent, prepared from magnesium and methyl iodide, was taken. The yield of (p-chlorophenyl)methyltrimethylsilane was 8.1 g (85%), b.p. 219-220° (746 mm), n_D^{20} 1.5125, d_4^{20} 0.9910, MR_D 60.12; calc. 59.36.

Found %: C 60.78, 60.66; H 7.58, 7.79; Si 13.75, 13.57. $C_{10}H_{15}SiCl$. Calculated %: C 60.48; H 7.56; Si 14.11.

3. β-Phenylethyltrichlorosilane. For reaction was taken 32.5 g of β-chloroethyltrichlorosilane, 78 g of benzene and 4 g of aluminum chloride. Half of the benzene (39 g) and the $AlCl_3$ were placed in the flask. The solution of the β-chloride in 39 g of benzene was added in 30 minutes with vigorous stirring. The reaction began immediately at 20° and continued without further self-heating for 33 hours. If the reaction is run at 80°, then the hydrogen chloride evolution is already complete in 3-4 hours. Then the $AlCl_3$ was removed by filtration as the complex with $POCl_3$ (0.03 mole), and the filtrate was distilled. The yield of β-phenylethyltrichlorosilane was 32.5 g (83%), b.p. 240.5° (739 mm), n_D^{20} 1.5188, d_4^{20} 1.2395, MR_D 58.57; calc. 58.04.

The β-phenylethyltrichlorosilane (11.5 g) was methylated with 0.2 mole of CH_3MgI. The yield of β-phenylethyltrimethylsilane was 6.9 g (78%), b.p. 210-211° (744 mm), n_D^{20} 1.4874, d_4^{20} 0.8650, MR_D 59.09; calc. 59.15.

Found %: C 74.39, 74.20; H 10.51, 10.45; Si 15.00, 15.13. $C_{11}H_{18}Si$. Calculated %: C 74.16; H 10.11; Si 15.73.

4. β-(p-Tolyl)ethyltrichlorosilane. For reaction was taken 30.0 g of β-chloroethyltrichlorosilane, 92 g of toluene and 4 g of aluminum chloride. The reaction was run under the conditions of Experiment 3 and was ended after 32 hours. Distillation gave 28.8 g (72% yield) of β-(p-tolyl)ethyltrichlorosilane, b.p. 121.5-122° (13 mm), n_D^{20} 1.5178, d_4^{20} 1.2129, MR_D 63.18; calc. 62.67.

The $CH_3C_6H_4CH_2CH_2SiCl_3$ (23.2 g) was methylated with CH_3MgI (0.36 mole). The yield of β-(p-tolyl)-ethyltrimethylsilane was 13.3 g (76%), b.p. 223-224° (748 mm), n_D^{20} 1.4880, d_4^{20} 0.8642, MR_D 63.93; calc. 63.78.

Found %: C 75.12, 75.38; H 10.64, 10.59; Si 13.73, 14.06. $C_{12}H_{20}Si$. Calculated %: C 75.53; H 10.55; Si 14.52.

5. β-(p-Chlorophenyl)ethyltrichlorosilane. For reaction was taken 100 g of β-chloroethyltrichlorosilane, 224 g of chlorobenzene and 15.8 g of aluminum chloride. The reaction was run under the conditions of Experiment 3 and was ended after 50 hours. Distillation gave 113.2 g (77% yield) of β-(p-chlorophenyl)ethyltrichlorosilane, b.p. 260-261° (752 mm), n_D^{20} 1.5310, d_4^{20} 1.3450, MR_D 63.02; calc. 62.88.

The β-(p-chlorophenyl)ethyltrichlorosilane (50 g) was methylated with 0.63 mole of CH_3MgI. The yield of β-(p-chlorophenyl)ethyltrimethylsilane was 30.0 g (75%), b.p. 127-128° (70 mm), n_D^{20} 1.5026; d_4^{20} 0.9767, MR_D 64.24; calc. 63.74.

Found %: C 62.44, 62.48; H 8.04, 8.02; Si 13.01, 12.95. $C_{11}H_{17}SiCl$. Calculated %: C 62.26; H 8.02; Si 13.20.

6. Diphenyltrichlorosilylmethane. a) For reaction was taken 43 g of dichloromethyltrichlorosilane, 78 g of benzene and 5.3 g of aluminum chloride. The reaction was run under the conditions of Experiment 1. However, despite the high temperature (80-85°) and heating for 150 hours, reaction was not observed here. Distillation gave 34.7 g of unchanged dichloromethyltrichlorosilane with b.p. 141-143°.

b) For reaction was taken 108 g of dichloromethyltrichlorosilane, 156 g of benzene and 41 g of aluminum chloride. The reaction was run under the conditions of Experiment 1. The evolution of hydrogen chloride was observed for 60 hours, after which it was practically nil. Distillation gave 33.1 g of dichloromethyltrichlorosilane with b.p. 140-142° (752 mm) and 14.3 g (13.7% yield, based on reacted chloride) of diphenyltrichlorosilylmethane, b.p. 167.5-168° (9 mm), m.p. 57-58°. The diphenyltrichlorosilylmethane, (14 g) was methylated with 0.15 mole of CH_3MgI. After suitable treatment there was obtained 7.5 g (67%) of diphenyltrimethylsilylmethane, b.p. 175-176° (14 mm), m.p. 70.5°.

Found %: C 80.08, 80.06; H 8.29, 8.37; Si 11.70, 11.48. $C_{15}H_{20}Si$. Calculated %: C 80.00; H 8.33; Si 11.67.

7. β-Phenylethylethyldichlorosilane. For reaction was taken 57 g of β-chloroethylethyldichlorosilane, 78 g of benzene and 2.6 g of aluminum chloride. The aluminum chloride and 39 g of benzene was placed in the flask. The chloride solution in 39 g of benzene was slowly added with stirring of the reaction mixture. The addition was made over 2 hours, since the immediate reaction was quite vigorous. The temperature of the reaction mixture was kept at 30° (regulated by the addition rate). Then the stirring was continued for another 8 hours. The reaction was completely ended in this time. The mixture was treated with 0.02 mole of $POCl_3$ and then heated to 50° for 30 minutes. Then the precipitate was filtered, and the filtrate was distilled. Distillation gave 23.6 g (34% yield) of β-phenylethylethyldichlorosilane, b.p. 126-127° (4 mm), n_D^{20} 1.5135, d_4^{20} 1.1109, MR_D 63.06; calc. 63.04.

Found %: C 51.92, 51.98; H 6.08, 6.11; Si 11.73, 11.88. $C_{10}H_{14}SiCl_2$. Calculated %: C 51.72; H 6.03; Si 12.07.

8. Attempts to Alkylate Benzene with Bis(Trichlorosilyl)chloromethane. a) For reaction was taken 53 g of bis(trichlorosilyl)chloromethane, 78 g of benzene and 5.3 g of aluminum chloride. The reaction was run under the conditions of Experiment 1. However, despite the high temperature of 80-90° that was used and the long reaction time of 80-100 hours, reaction was not observed here. After suitable treatment and distillation there was isolated 42 g of unchanged bis(trichlorosilyl)chloromethane with b.p. 210-212° (756 mm).

b) The amount of aluminum chloride was increased in the second experiment. For reaction was taken 40 g of bis(trichlorosilyl)chloromethane, 78 g of benzene and 26.6 g of aluminum chloride. The reaction was run under the conditions of Exp. 1. However, even with the larger amount of aluminum chloride, the reaction failed to proceed. Distillation gave 34 g of unchanged bis(trichlorosilyl)chloromethane with b.p. 210-213° (753 mm).

9. Oxidation of β-Tolylethyltrimethylsilane. In a round-bottomed flask, fitted with reflux condenser, was placed 10 g of β-tolylethyltrimethylsilane and 15 ml of nitric acid (d 1.110). The flask contents were boiled for 50 hours. A considerable amount of crystals was formed. On conclusion of reaction the organic layer and crystals were separated; the water layer was extracted with ether. The ether extract was combined with the organic layer, and the ether was evaporated. The remaining investigation of the obtained reaction products was made by the method of A. F. Dobryansky and R. D. Obolentsev [9]. There was isolated 5.5 g of crystalline terephthalic acid. Other acids were not found.

10. Oxidation of β-(Chlorophenyl)ethyltrimethylsilane. A mixture of 8 g of β-(chlorophenyl)ethyltrimethylsilane and 10 ml of nitric acid (d 1.110) was placed in a round-bottomed flask. The reaction mixture was boiled for 50 hours. Then the crystals obtained here were separated, and the water layer was extracted with hot benzene. The benzene extract and crystals were combined, and the benzene was evaporated. The precipitate was recrystallized from benzene. The yield of p-chlorobenzoic acid with m.p. 241° was 3.9 g. The mixed melting point failed to be depressed. Other acids were not obtained.

11. Reaction of β-Chloroethyltrichlorosilane with Aluminum Chloride. In the pot of a rectification column (~ 30 theoretical plates) was placed 98 g of β-chloroethyltrichlorosilane and 1 g of $AlCl_3$. The pot was heated and the fraction up to 95° was collected. Then the still was put on total reflux, and the temperature of the refluxing liquid dropped to 89° due to the formation of some vinyltrichlorosilane, after which the fraction up to 95° was again collected. If the temperature of the refluxing liquid under total reflux failed to drop, then another gram of $AlCl_3$ was added to the still pot. These operations were repeated until only a hard black residue (which readily dissolved in alkali) remained in the still pot. The distillate obtained here was distilled again, and the following fractions were collected: 10.3 g of silicon tetrachloride, b.p. 56.5-57°, and 56.8 g of vinyltrichlorosilane (70% yield), b.p. 89.5°, n_D^{20} 1.4365.

12. Reaction of α-Chloroethyltrichlorosilane with Aluminum Chloride. In the pot of a rectification column (~ 30 theoretical plates) was placed 98 g of α-chloroethyltrichlorosilane and 1 g of $AlCl_3$. The reaction was run the same as indicated in the previous paragraph. The redistillation of the rectificate gave: 32.8 g of silicon tetrachloride, b.p. 56.5-57°, and 38.4 g (48% yield) of vinyltrichlorosilane, n_D^{20} 1.4362.

SUMMARY

1. The possibility for the silicoalkylation of aromatic compounds with α- and β-chloroalkylsilane chlorides in the presence of $AlCl_3$ was shown. The reactivity of the chloroalkylsilane chlorides in the silicoalkylation reaction as a function of their structure was investigated.

2. The reaction of α- and β-chloroethyltrichlorosilanes with aluminum chloride was studied and it was

shown that in both cases vinyltrichlorosilane (in respective yields of 48 and 70%) and silicon tetrachloride are formed.

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ACYLATION OF AROMATIC AMINES WITH MALEIC ANHYDRIDE

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The acylation of arylamines with maleic anhydride was first realized by Anschutz [1], who obtained N-phenylmaleamic acid from aniline and maleic anhydride. Then Auwers and coworkers [2], and later Freeman [3], repeated this reaction. A number of other N-arylmaleamic acids were also synthesized [4-6].

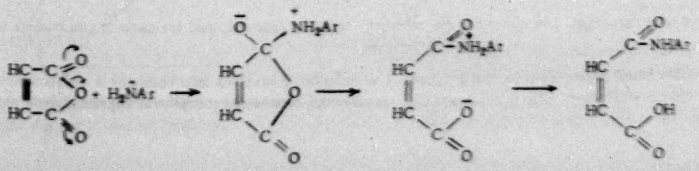
The reaction of maleic anhydride with aromatic amines has been insufficiently studied. The derivatives of the N-arylmaleamic acids have been studied with especial rarity. In general, the kinetics and mechanism for the acylation of amines with maleic anhydride have not been studied. Data is found in the literature on the qualitative and quantitative aspects of the acylation reaction with phthalic anhydride [10-12]. Taking into consideration what has just been said, and the fact that the reaction studied by us possesses both theoretical and practical interest, we undertook its study.

The first stage of the work was to study the synthesis of N-arylmaleamic acids. From the literature it is known that the N-arylmaleamic acids can be obtained by the reaction of maleic anhydride with Schiff bases [4-6], and by the acylation of aromatic amines with maleic anhydride.

Most of the N-arylmaleamic acids described in the literature were synthesized from Schiff bases and maleic anhydride. This reaction, as we found out, does not always assure obtaining pure products and, in addition, is complicated. We settled on the second method as being more convenient and assuring high yields of the acids. In the synthesis of N-arylmaleamic acids from amines and maleic anhydride not only can the formation of the N-arylmaleamic acids be expected, but also the addition of the amines to the double bond of maleic anhydride. According to [13] the mixing of aqueous solutions of aniline and maleic acid gives phenylaspartic acid. In the acylation of aromatic amines with maleic anhydride in nonaqueous solvents we established that the indicated side reaction is either not observed at all or proceeds insignificantly. Only in the reaction with p-phenylenediamine could the presence of an addition product at the double bond be shown by chromatographic separation.

We qualitatively established at the start that the reaction rate for the acylation of amines with maleic anhydride depends, as was to be expected, on their basicity. For exact elucidation of the influence of amine basicity and to obtain data on the mechanism of the reaction we studied the kinetics of acylating amines of different basicity.

The acylation reaction belongs to the class of electrophilic-nucleophilic reactions, in which the role of the electrophilic agent is played by the acid anhydride, and that of the nucleophilic agent by the amine. In the maleic anhydride molecule, due to the drawing away of electrons from the carbon atom by the oxygen of the carbonyl group, and also by the oxygen of the anhydride bond, a certain positive charge appears on the carbon atom, and since the amine molecule contains a nitrogen atom with an unshared pair of electrons, then the following primary reaction appears most probable.



The internal salt of the betaine type that is formed here suffers subsequent transformations: a proton from the nitrogen atom migrates to the oxygen atom, negatively charged, and as a result the N-arylmaleamic acid is obtained. The indicated migration is conditioned by the fact that there is a very pronounced decrease in basicity when the acyl group is introduced into the amine molecule, as a result of which the corresponding ion, formed by the addition of the proton to the acylamino group, becomes strongly acidic. This assures transfer of the proton from the nitrogen atom to the carboxyl ion. The end result is the formation of the undissociated acid molecule. The transitions by the indicated equation are completed quite rapidly in the majority of cases, since this is facilitated by the spatial proximity of the carboxyl anion and ammonium group. The validity of such a conclusion is supported by the fact that the energy of activation values, calculated by us from experimental data, for the acylation of amines with maleic anhydride are relatively low: for the acylation of p-aminoazobenzene 1680, o-chloroaniline 3200, p-chloroaniline 7670, and m-nitroaniline 4790 cal./mole. From the presented data it follows that the rate of the acylation reaction will be determined by the rate of the primary act of amine addition to the anhydride molecule, which in turn depends on the basicity of the amine. As a measure of the basic nucleophilic properties of the amine it is most convenient to take the negative logarithm of the hydrolysis constant pK' of the arylammonium salt, which is related to the usually presented constant pK_B in the following manner:

$$pK' = pK_{H_2O} - pK_B \text{ or } 13.92 - pK_B \text{ (for 25°).}$$

As soon as we started running the syntheses we found that the rate for the acylation of aromatic amines depends on the nature of the substituents of the arylamines. At times the reaction rate was retarded considerably with decrease in amine basicity. To establish the exact relationship existing between the rate for the acylation of arylamines and their basicity we studied the kinetics of the reaction on 8 aromatic amines with pK' ranging from 2.52 to 4.58. The reaction rates were measured at + 10°, and for some of the amines at + 20 and + 30°, by the method of determining the acidity of the reaction mass by titration with 0.1 N alkali.

As a result of studying the kinetics of the reaction for the acylation of amines we established that the reaction is bimolecular and is defined by the equation:

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)},$$

where a is the initial concentration of maleic anhydride, and x is the number of moles of the N-arylmaleamic acid, formed to the time t from the start of reaction. The amount of N-arylmaleamic acid formed was determined by titrating the reaction mixture in the presence of phenolphthalein, with the assumption that 1 equivalent of acid disappears with the formation of the N-arylmaleamic acid. After substitution the equation assumed the following form:

$$k = \frac{1}{t} \cdot \frac{20W}{\beta V_0} \cdot \frac{V_0 - V}{V - \frac{V_0}{2}} \text{ liter/mole. min.,}$$

where W is the volume of the sample taken after mixing the maleic anhydride and amine samples, V_0 is the volume in milliliters of 0.1 N alkali with normality coefficient β, consumed in the titration of volume W at the moment of mixing, and V is the volume of 0.1 N alkali, consumed in the titration of volume W after time t.

The initial maleic anhydride concentration is: $a = \frac{0.1\beta V_0}{2W}$. The number of moles of N-arylmaleamic acid formed, corresponding to the reduction in acidity, is $x = \frac{0.1\beta}{W}(V_0 - V)$.

As can be seen from Figs. 1-4, the ratio $\frac{1}{t} \cdot \frac{V_0 - V}{V - \frac{V_0}{2}}$ remains constant, and for each of our studied amines the experimentally found points lie on a straight line. The calculated reaction rate constant is constant within the limits of experimental error. This is evidence that actually the rate of the reaction is expressed by a second order equation.

It was also experimentally verified by us that a relationship exists between the rate of the acylation reaction and the basicity of the amines: it was found that the logarithm of the rate constant of the acylation reaction is a linear function of the negative logarithm of the hydrolysis constant pK' of the amine salt. The rate constant of the reaction increases with increase in the basicity of the amines, as can be seen from Fig. 5.

The energy of activation was calculated on the basis of kinetics data, obtained at 20 and 30° by means of Arrhenius equation:

$$D = \log \frac{k_2}{k_1} \; 2.3026R \left(\frac{T_1 T_2}{T_2 - T_1} \right) .$$

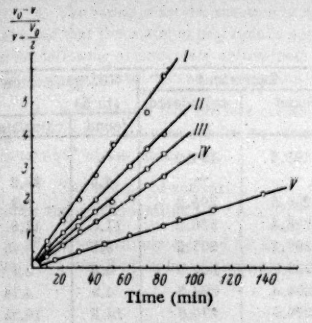


Fig. 1. Acylation at 10°.
I) Aniline, II) o-anisidine, III) o-toluidine, IV) β-naphthylamine, V) p-chloroaniline.

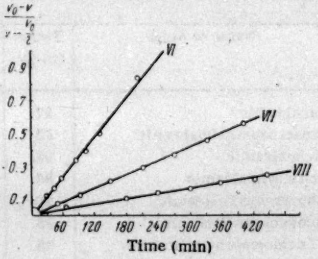


Fig. 2. Acylation at 10°.
VI) p-Aminoazobenzene, VII) o-chloroaniline, VIII) m-nitroaniline.

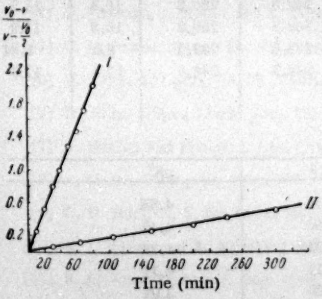


Fig. 3. Acylation at 20°.
I) p-Chloroaniline, II) o-chloroaniline.

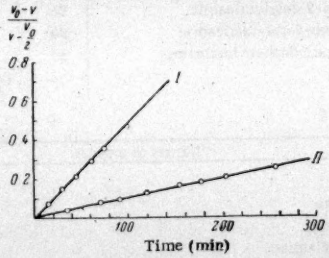


Fig. 4. Acylation at 30°.
I) p-Aminoazobenzene, II) m-nitroaniline.

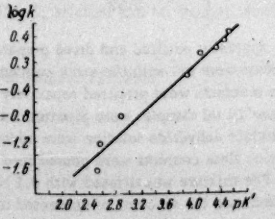


Fig. 5. Relation between log K of the reaction rate and the degree of amine basicity.

EXPERIMENTAL

Synthesis of N-Arylmaleamic Acids. A solution of maleic anhydride in an organic solvent, most frequently benzene, and at times either chlorobenzene or acetone, was added (with mechanical stirring) to a solution of the amine (in the same solvent), contained in a three-necked reaction flask, fitted with stirrer, reflux condenser and thermometer. The reagents were taken in nearly equimolar amounts with a 10% excess of maleic anhydride. Depending on the basicity of the amine, the reaction mixture was kept for a certain length

of time at either room or slightly elevated temperature. The end of reaction was determined with the aid of p-dimethylaminobenzaldehyde. If unreacted amine is present in the reaction medium, then it forms either a yellow or orange coloration with p-dimethylaminobenzaldehyde.

The N-arylmaleamic acid obtained after cooling the reaction mass, was filtered, washed, either precipitated from alkaline solution or recrystallized from alcohol, dried, and analyzed.

To determine the acid equivalent a weighed sample was titrated with 0.1 N alkali in the presence of phenolphthalein, while the nitrogen was determined by the Kjeldahl method. The method just described for the preparation of N-arylmaleamic acids is the simplest and most convenient. The acids synthesized by us are summarized in Table 1.

TABLE 1

Name of Acids	Yield (in %)	Melting point	Equivalent		Nitrogen content (in %)	
			found	calculated	found	calculated
N-Phenylmaleamic	97	198-199°	190.6	191.2	—	—
N-p-Benzeneazophenylmaleamic	93	208-209	—	—	14.4	14.2
N-m-Tolylmaleamic	98	167	205.5	205.2	6.5	6.8
N-o-Nitrophenylmaleamic	96	134	236.4	236.2	11.5	11.8
N-m-Hydroxyphenylmaleamic	96	185	207.1	207.2	6.5	6.76
N-2,5-Dichlorophenylmaleamic	95	143	259.9	260.1	5.6	5.4
N-2,4,5-Trichlorophenylmaleamic	95	162	294.4	294.5	4.9	4.74
N-4-Chloro-2-nitrophenylmaleamic	94	109-110	270.9	270.6	10.3	10.35
N-5-Nitro-2-methoxy-4-tolylmaleamic	92	135-136	280.5	280.6	9.6	10.0
N-2-Nitro-4-ethoxyphenylmaleamic	94	137-138 (with decomp.)	280.2	280.6	9.9	10.0
N-3-Nitro-4-tolylmaleamic	92	126	249.6	250.2	10.9	11.2
N-5-Nitro-2-tolylmaleamic	95	154	249.3	250.2	10.8	11.2
N-4-Chloro-2-tolylmaleamic	93	129-130	238.5	239.6	6.1	5.84
N-4-Acetamidophenylmaleamic	95	218 (with decomp.)	246.9	248.0	11.1	11.3

TABLE 2

Names of amines	log k	pK*
Aniline	+ 0.46	4.58
o-Anisidine	+ 0.30	4.49
o-Toluidine	+ 0.21	4.39
β-Naphthylamine	+ 0.14	4.11
p-Chloroaniline	− 0.20	3.92
p-Aminoazobenzene	− 0.80	2.90
o-Chloroaniline	− 1.25	2.57
m-Nitroaniline	− 1.64	2.52

Kinetics of Maleic Anhydride Reaction with Aromatic Amines. Specially purified and dried preparations were used to study the kinetics of the acylation reaction. The experiments were run with the same concentrations for the amine and maleic anhydride (0.025 mole). The solutions of the reactants were prepared separately and kept at a constant temperature in a thermostat. From the amine solutions 10 ml samples were pipetted into reaction flasks, contained in the thermostat, and then 10 ml aliquots of maleic anhydride solution were added to each flask. After the lapse of a predetermined length of time the reaction flask contents were poured into boiling water to hydrolyze any unreacted anhydride and kill the reaction. The mixture was titrated with 0.1 N alkali solution in the presence of phenolphthalein, the acidity determined, and the amounts of unreacted maleic anhydride and formed N-arylmaleamic acid calculated. Graphs, expressing the relation between $\frac{V_0 - V}{V - \frac{V_0}{2}}$ and time (Figs. 1-4), were constructed on the basis of the experimental data obtained for the kinetics of the acylation.

As can be seen from the data given in Table 2, the calculated rate constants for the acylation of arylamines decrease with reduction in the degree of basicity shown by the amines.

SUMMARY

1. The reaction of maleic anhydride with aromatic amines was studied and its most probable mechanism was presented.

2. The addition of amines to the double bond of maleic anhydride fails to take place when the reaction is run in nonaqueous solvents.

3. The kinetics for the reaction of aromatic amines with maleic anhydride in benzene was studied. It was found that the reaction proceeds in accord with the second order equation and the reaction rate constants for the following amines were determined: aniline, o-anisidine, o-toluidine, β-naphthylamine, p-chloroaniline, p-aminoazobenzene, o-chloroaniline and m-nitroaniline.

4. It was shown that the rate constants increase with increase in amine basicity. It was found that the logarithm of the rate constant for the reaction is a linear function of the negative logarithm of the hydrolysis constant pK' of the amine salt.

5. The energy of activation values for the acylation of p-chloroaniline, p-aminoazobenzene, o-chloroaniline and m-nitroaniline were calculated.

6. A very simple method for the synthesis of N-arylmaleamic acids from maleic anhydride and aromatic amines was verified on many amines.

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BUTYROLACTONE AND ITS DERIVATIVES

I. OXIDE CONDENSATIONS – SYNTHESIS OF BUTYROLACTONE DERIVATIVES

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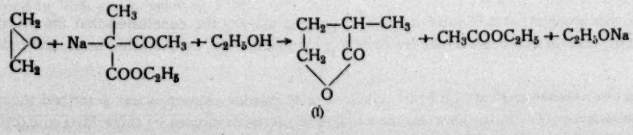
In recent years great interest has appeared toward butyrolactone and its derivatives. On the one hand this is due to the fairly wide distribution of natural-occurring products in whose composition the five-membered lactone ring is present, and on the other hand it is due to the constantly increasing importance of butyrolactone and its derivatives in the chemical industry. This importance increased greatly from the time that butyrolactone itself became commercially available [1].

One of the oldest methods for the synthesis of compounds containing the five-membered lactone ring is the condensation of organic α-oxides with malonic and β-ketocarboxylic esters – the oxide condensations. As early as 1899 the first examples of oxide condensations were described by Traube and Lehmann [2]. In subsequent years different authors described numerous variations of these reactions, of which the condensation of ethylene oxide with acetoacetic ester [3] and of ethylene oxide with alkylated malonic esters [4] found industrial use. However, despite the passage of some 50 years since the first studies in this field were made, the limits for the application of oxide condensations were never fully elucidated. In particular, the examples of condensing α-oxides with monoalkylated β-dicarbonyl compounds proved to be insufficiently studied. If the behavior of the monoalkylated malonic esters in this reaction was studied in fairly great detail by Rothstein [4], then with respect to the monoalkylated acetoacetic esters this reaction remained very superficially studied by Traube and Lehmann [5].

The problem of the present work was to make a more detailed study of oxide condensations involving the participation of those β-keto esters in which only one labile hydrogen atom is present.

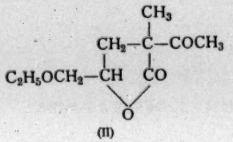
The first experiments showed that in these cases the reaction proceeds somewhat differently and does not lead to obtaining the anticipated α-alkyl-α-acyl derivatives of butyrolactone. Sodio-α-methylacetoacetic ester reacts vigorously with ethylene oxide in alcohol solution with the formation of equivalent amounts of ethyl acetate and α-methylbutyrolactone (I), first described by Fichter and Herbrand [6]. The expected α-methylacetylbutyrolactone failed to be formed at all. Consequently, the condensation of an α-alkylated acetoacetic ester with ethylene oxide, in contrast to the condensation of the unsubstituted ester, is accompanied by the cleavage of the acetyl group as an ester and proceeds in accord with the scheme:



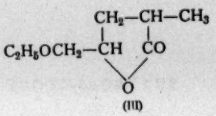
(I)

The results obtained by us contradict the data of Traube and Lehmann [5], who found that acylated lactones are obtained in the condensation of α-methyl and α-ethylacetoacetic esters with epichlorohydrin under such conditions. However, the authors themselves do not consider the structure of the compounds obtained by them

as being proved, all the more so since their elementary analysis results were insufficiently satisfactory. For example, on comparing the values obtained by Traube and Lehmann with those required by theory for the acylated (II) and not acylated (III) lactone from α-methylacetoacetic ester, it is difficult to decide as to the composition of the obtained compound.



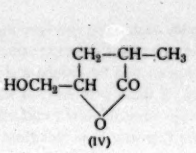
(II)



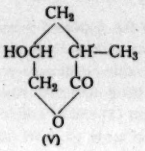
(III)

Found %: C 60.03, 59.80; H 8.81, 8.85. (II) ($C_{10}H_{16}O_4$). Calculated %: C 60.00; H 8.00. (III) ($C_8H_{14}O_3$). Calculated %: C 60.71; H 8.92.

A repetition of the experiments made by Traube and Lehmann revealed that they had arrived at erroneous conclusions. Here also the reaction proceeds with the formation of ethyl acetate, which is obtained together with a substance having b.p. 163-167° (17 mm). From the elementary analysis data this substance has the composition $C_6H_{10}O_3$, contains a hydroxyl group (forms an ester with 3,5-dinitrobenzoyl chloride), shows neutral reaction and contains the lactone ring, shown by titration with alkali at 60°. From its properties and method of preparation the substance can be either α-methyl-δ-hydroxy-γ-valerolactone (IV) or α-methyl-γ-hydroxy-δ-valerolactone (V):



(IV)



(V)

The probable generality of the scheme for the preparation of the hydroxylactone with other examples of oxide condensations speaks in favor of structure (IV), while the tendency shown by the substance to polymerize, characteristic of a δ-valerolactone, speaks in favor of structure (V) •.

The results of the described experiments lead to the conclusion that the condensation of an α-alkylated acetoacetic ester is accompanied by cleavage of the acetyl group. It is natural to assume that this proceeds due to alcoholysis of the initially formed α-acyl-α-alkylbutyrolactone by the sodium alcoholate in alcohol medium. ••

For the purpose of verifying this postulation we ran some experiments on the condensation of ethylene oxide with sodio-α-methylacetoacetic ester in nonpolar solvents. It was found that ethylene oxide fails to react with the sodium derivatives of the keto ester in either ether or toluene, in the temperature limits of from room temperature to 100°. We were able to run the condensation in the absence of solvent, but under the conditions of the Perkin reaction. The prolonged heating (for many hours) at 110° of a mixture of α-methylacetoacetic ester, ethylene oxide and potassium acetate results in the formation of α-methylbutyrolactone and an equivalent amount of ethyl acetate.

In principle this observation is of interest, since it permits making the conclusion that the primary processes of the Perkin reaction and of oxide condensations have much in common. On the other hand, the indicated

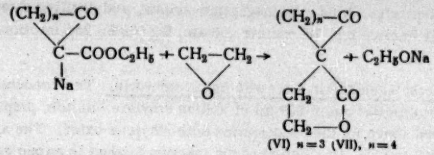
• The preparation by another method of a hydroxylactone with similar properties was described recently [8]. The authors assign structure (IV) to it, however, the method of preparation used by them fails to exclude structure (V).

•• However, such an assumption is contradictory to the results of the condensation experiments with epichlorohydrin, where sodium ethylate is not formed at all.

observation makes highly improbable the above-expressed postulation that alcoholysis is the reason for the cleavage of the acyl group in oxide condensations of the alkylated keto esters.

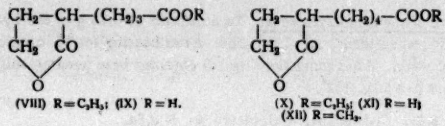
This new variation for the running of oxide condensations deserves consideration because of its simplicity and the excellent results obtained. While in the condensation with sodium ethylate the yield of α-methylbutyrolactone is only 50%, with potassium acetate the yield reaches 70-80%.

The oxide condensations proceed in a similar manner for the cyclic analogs of the α-alkylacetoacetic esters, namely, for 2-carbethoxycyclopentanone and 2-carbethoxycyclohexanone. Instead of the "normal" reaction course by the scheme



(VI) n = 3 (VII), n = 4

with the formation of the spiro-ketolactones (VI) and (VII), the reaction is accompanied by deacylation and the formation of: in the first case – the lactono ester of α-(β-hydroxyethyl) adipic acid (VIII), and in the second case – the lactono ester of α-(β-hydroxyethyl)-pimelic acid (X).



(VIII) R = C_2H_5; (IX) R = H. (X) R = C_2H_5; (XI) R = H; (XII) R = CH_3.

The lactono ester (VIII) was obtained by Pakendorf and Machus in 1941 [7] by the condensation of 2-carbethoxycyclopentanone with ethylene oxide in the presence of piperidine. This work is of interest as an example of the extension of the Knoevenagel reaction conditions to oxide condensations. However, the authors failed to elucidate whether opening of the cyclopentane ring is specific for these conditions, or whether such a reaction course is inherent to all cyclic β-keto esters.

The lactono ester (VIII) is formed in 30-40% yield, irrespective of whether sodium ethylate or potassium acetate is used in the condensation. In the latter case, together with the lactono ester, the ester of adipic acid is formed in an amount of 0.10-0.15 equivalents. The reasons and mechanism for its formation still remain obscure.

The lactono ester (VIII) is saponified when boiled with dilute sulfuric acid, forming the lactono acid (IX), characterized by a number of derivatives.

The condensation of 2-carbethoxycyclohexanone with ethylene oxide proceeds satisfactorily in methanol, which, apparently, is explained by the greater solubility of the sodium derivative of the keto ester in it. When the mixture of lactono esters (X) and (XII) obtained here is saponified with dilute sulfuric acid the lactono acid (XI) is formed in 25% yield, based on starting keto ester. With diazomethane the lactono acid forms the methyl ester (XII).

EXPERIMENTAL

Condensation of α-Methylacetoacetic Ester with Ethylene Oxide. a) To a solution of 3.3 g of sodium in 50 ml of anhydrous alcohol, cooled to −3°, was added with shaking 20 g of α-methylacetoacetic ester and 7 g of ethylene oxide. For the next 4 hours the temperature of the periodically shaken mixture was maintained at 30-40° by external cooling. The resulting solution was allowed to stand 12 hours, the solvent was vacuum-distilled (in a 40° bath), and the amount of ethyl acetate in the distillate (42 g) was determined. Found 0.069 mole of $CH_3COOC_2H_5$ (49.3%).

The residue after distilling off the solvent was decomposed with a mixture of 7 g of concentrated sulfuric acid and 30 g of ice, the sulfate was separated, and the filtrate was extracted with ether in a perforator. The neutralized and dried extract was evaporated. The residue was vacuum-distilled (18 mm). Two fractions were collected: 1st fraction up to 90°, being unreacted α-methylacetoacetic ester (10 g); 2nd fraction 94-96°, being α-methylbutyrolactone, 7 g (50%). The latter was a colorless liquid, b.p. 201-202°, readily soluble in water, shows neutral reaction, and titrates with alkali when heated.

n_D^{20} 1.4311, d_4^{20} 1.0500, MR_D 24.66; calc. 24.74.

b) A mixture of 14.4 g of α-methylacetoacetic ester, 4.5 g of ethylene oxide and 5 g of anhydrous potassium acetate was heated in a sealed tube for 8 hours at 110°. The reaction mixture was diluted with 10 ml of water, the top layer was separated, dried over magnesium sulfate, and distilled through a short column. Two fractions were collected: 1st fraction b.p. 78° – ethyl acetate, 6 g (68%); 2nd fraction b.p. 201-202° – α-methylbutyrolactone, 7 g (70%).

Condensation of α-Methylacetoacetic Ester with Epichlorohydrin. The condensation of 43 g of the keto ester with 28 g of epichlorohydrin was run in 200 ml of sodium ethylate solution, prepared from 6.9 g of sodium, under the conditions described above for the condensation with ethylene oxide. The amount of ethyl acetate in the vacuum-distilled solvent was 81%. Distillation of the reaction product in vacuo gave two fractions: 1st fraction 10 g – α-methylacetoacetic ester, and 2nd fraction 5 g, b.p. 163-167° – either hydroxylactone (IV) or (V). •

n_D^{20} 1.4548, d_4^{20} 1.1209, MR_D 31.45; calc. 30.90.

Found %: C 56.10, 56.04; H 7.90, 8.03. $C_6H_{10}O_3$. Calculated %: C 55.45; H 7.70.

3,5-Dinitrobenzoate of the Hydroxylactone. To a mixture of 0.26 g of the hydroxylactone and 0.5 g of 3,5-dinitrobenzoyl chloride was added 1 ml of pyridine. After heating for 15 minutes at 50-60° the mixture was diluted with 10 ml of water. After some time the oil obtained here became solid. After recrystallization from alcohol the substance had m.p. 112°.

Found %: N 8.83, 8.85. $C_{13}H_{12}O_8N_2$. Calculated %: N 8.64.

Condensation of 2-Carbethoxycyclopentanone with Ethylene Oxide. 1) A mixture of 15.6 g of the keto ester, 5 g of ethylene oxide and 25 ml of anhydrous alcohol was mixed at −2° with a solution of 2.3 g of sodium in 40 ml of alcohol. For the next 2.5 hours the temperature of the self-heating mixture was maintained at 20-25° by external cooling, and then the resulting solution was kept at room temperature for 12 hours. The solvent was vacuum-distilled at 45°, the residue decomposed with 10% acetic acid and ice, and the separated oil was extracted with benzene. From the residue after distilling off the solvent there was isolated at 7 mm a fraction, boiling at 168-172°, and weighing 7 g (VIII). The substance is a colorless viscous liquid, mixes with the ordinary organic solvents, but is difficultly soluble in water; when heated it combines with 2 equivalents of alkali.

B.p. 164-166° at 5 mm, n_D^{20} 1.4562, d_4^{20} 1.1025, MR_D 49.36; calc. 49.49.

Found %: C 60.00, 60.02; H 7.98, 8.09. Equiv. 99.6. $C_{10}H_{16}O_4$. Calculated %: C 60.00; H 8.05. Equiv. 100.0.

2) A mixture of 31 g of the keto ester, 8.8 g of ethylene oxide and 3 g of anhydrous potassium acetate was heated in a sealed tube at 120° for 4 hours. The tube's contents were diluted with water until the precipitate dissolved. The oil obtained here was dried, having been diluted with ether, and then was vacuum-distilled. Two substances were obtained: 1) diethyl adipate, 5.7 g (14%), b.p. 132-136° at 18 mm, and 2) lactone (VIII), 15 g (37%), b.p. 163-166° at 5 mm.

Saponification of the Lactono Ester (VIII). A mixture of 8 g of (VIII) and 40 ml of 5% sulfuric acid was boiled for 30 minutes. The solution obtained here was neutralized to Congo with soda and evaporated nearly to dryness. The residue was extracted with 250 ml of hot benzene, the extract evaporated to half volume and then kept at 5° for 12 hours. The lactono acid (IX) precipitated here, 3.4 g, and was recrystallized twice from benzene.

Colorless needles, m.p. 82-83°, readily soluble in hot benzene, difficultly soluble in ether and in cold benzene, and quite readily soluble in water.

• A considerable portion of the substance polymerized during distillation.

Found %: C 55.88; H 7.16. Equiv. 171.6. $C_8H_{12}O_4$. Calculated %: C 55.78; H 7.03. Equiv. 172.1.

Condensation of 2-Carbethoxycyclohexanone with Ethylene Oxide. The condensation of 25.5 g of the keto ester and 14 g of ethylene oxide in a solution of 3.4 g of sodium in 60 ml of methanol was run under the same conditions as described above for the 2-carbethoxycyclopentanone. In addition to 9.5 g of unchanged keto ester there was obtained 10 g of an oily substance, boiling at 0.2 mm in the range 120-135°. Without further purification the substance was saponified by boiling with 25 ml of 5% sulfuric acid. The lactono acid (XI), obtained after cooling, was recrystallized twice from benzene. Colorless needles, m.p. 84-85°; readily soluble in hot benzene and alcohol, and poorly soluble in cold benzene and water.

Found %: C 57.83; H 7.79. Equiv. 185.0. $C_9H_{14}O_4$. Calculated %: C 58.03; H 7.58. Equiv. 185.1.

Acid Chloride of (IX). Obtained from the acid and thionyl chlorides at 100°. Oily liquid with a weak disagreeable odor, b.p. 140-141° at 0.5 mm, n_D^{20} 1.4808.

Found %: Cl 18.72. $C_{18}H_{11}O_3Cl$. Calculated %: Cl 18.61.

Diphenylamide of (IX). Obtained from the acid chloride and diphenylamine in benzene. Colorless leaflets, m.p. 142-143°.

Found %: N 4.60. $C_{20}H_{21}O_3N$. Calculated %: N 4.33.

Silver Salt of (IX). Glistening leaflets from water; decomposes without melting when heated.

Found %: Ag 38.65. $C_8H_{11}O_4Ag$. Calculated %: Ag 38.70.

Methyl Ester of (IX). Obtained from the silver salt and methyl iodide in benzene at 100°. Oily liquid with a slight odor.

B.p. 135-136° at 0.2 mm, n_D^{20} 1.4583, d_4^{20} 1.1390, MR_D 44.63; calc. 44.87.

Found %: C 57.76; H 7.35. $C_9H_{14}O_4$. Calculated %: C 57.99; H 7.58.

Methyl Ester (XII). Obtained from the acid (XI) and a 5% ether solution of diazomethane. Practically odorless oily liquid.

B.p. 145-146° at 0.2 mm; n_D^{20} 1.4590, d_4^{20} 1.1114, MR_D 49.22; calc. 49.49.

Found %: C 60.05; H 8.13. $C_{10}H_{16}O_4$. Calculated %: C 60.00; H 8.05.

SUMMARY

1. The condensation of α-methylacetoacetic ester with ethylene oxide under the influence of sodium ethylate is accompanied by the cleavage of the acetyl group as ethyl acetate and leads to the formation of α-methylbutyrolactone.

2. The data of Traube and Lehmann on the condensation of α-alkylated acetoacetic esters with epichlorohydrin proved to be in error. Here also the reaction is accompanied by cleavage of the acetyl group.

3. Similar to the monoalkylated acetoacetic ester, the condensation of its cyclic analogs, 2-carbethoxycyclopentanone and 2-carbethoxycyclohexanone, proceeds by the same scheme.

4. A convenient variation of oxide condensations that possesses practical interest is the heating of the keto ester with ethylene oxide in the presence of anhydrous potassium acetate and in the absence of solvent (conditions of the Perkin reaction).

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SYNTHESIS OF NAPHTHALIMIDE

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In recent years naphthalimide has attracted the attention of chemists as an intermediate in the synthesis of anthanthrone, perylene and some other groups of dyes [1-4]. Even in the previous century it was obtained by Behr and Van-Dorp [5] and studied in detail by Joubert [6]. According to the patent issued to Jaeger [7], naphthalimide is obtained by the prolonged heating of sodium naphthalate with ammonium salts. In not one of the mentioned works is a detailed method or exact yield of the amide given. More recently a more complete study of this reaction was made by Soviet chemists [3, 8]. A. E. Porai-Koshits and I. S. Pavlushenko obtained naphthalimide in quantitative yield, while by the method proposed by V. M. Rodionov and A. M. Federova [9] the yield reaches 98%. Actually, all of the indicated yields are lower, since the authors calculated their yields on the basis of naphthalic acid, but instead they were working with the anhydride.

Incorrect statements exist in the literature on the conditions for converting naphthalic acid into the anhydride. Anselm and Zuckmayer [10] believed that naphthalic acid, free of the anhydride, can be obtained only by maintaining special conditions, since, in their opinion, the heat of reaction, liberated in the precipitation of naphthalic acid from its salt solutions, is sufficient to convert part of the acid into the anhydride. These authors were able to obtain hydroxynaphthalic acid only in the form of its anhydride. Most of the other authors believe that the anhydride can be obtained from naphthalic acid only by heating the latter to 150-180° and that the naphthalic acid, dried at 100-105°, is free of the anhydride. According to Quincke [11], nitronaphthalic acid is transformed into the anhydride at 140-150°.

Both of the indicated viewpoints proved to be erroneous. We established that naphthalic acid can be obtained free of moisture and anhydride if it is dried at a temperature not exceeding 15-17°. At a temperature of 30°, and more rapidly at 70°, it begins to be converted into the anhydride. At 99-100° the naphthalic acid is completely transformed into the anhydride. Consequently, the product that is dried to constant weight at about a temperature of 100° is not naphthalic acid, as a number of authors have assumed up to now, but instead is the anhydride. It should be added that at 150-180° the naphthalic anhydride begins to show considerable sublimation, and drying it at such a high temperature is clearly impractical.

We studied the conversion rate of the mono- and dinitro- naphthalic acids, and of the mono- and dichloronaphthalic acids, into their respective anhydrides. They are all completely transformed into the anhydrides even at about 100°. Of them the substituted naphthalic acids are transformed into anhydrides more rapidly than is naphthalic acid, the disubstituted acids are transformed more rapidly than the monosubstituted acids, and the chloro-substituted acids more rapidly than the nitro-substituted acids. In the course of 8 days at 27-30° the 4,5-dichloronaphthalic acid is completely transformed into the anhydride. In the same length of time the 4-chloro- and 4,5-dinitronaphthalic acids show 50% conversion into their respective anhydrides, the 4-nitronaphthalic acid shows 15% conversion, and naphthalic acid shows only 10%. All of these acids are completely transformed into their respective anhydrides at 100°.

The conditions for the conversion of naphthalic anhydride into the imide were checked by us, using all of the methods described in the literature. The method given in the Jaeger patent is somewhat tedious, the yield is lower than with other methods, and the imide is of poorer quality. The method of Rodionov and Fedorova can have only preparative significance. Only the method of directly heating naphthalic anhydride with aqueous ammonia solution at either atmospheric or elevated pressure can have technical application. The yield of the imide is practically the same in both cases. In the first case the apparatus assembly shows an advantage, in the second case there is a considerable conservation of time. The reaction for the formation

of the imide at atmospheric pressure was studied by us in detail. Under the optimum conditions the imide is obtained in 95-97% yield, based on anhydride taken for reaction, and in quantitative yield, if calculated on the basis of reacted anhydride. The temperature and length of heating show a greater influence on the imide yield than do the concentration (within the limits of 2-7%) and amount of ammonia.

EXPERIMENTAL

Naphthalic anhydride was dissolved in a 10-fold amount of 4% sodium hydroxide solution and the solution was acidified with hydrochloric acid. The naphthalic acid precipitate was filtered, washed with water, and dried at 13-17° to constant weight. The obtained acid (for its analysis see Table 1), after drying in a thermostat at 99-100° to constant weight, was completely converted into the anhydride. The latter was dried further at 148-150° for 15 hours. After each hour the product was placed for 20 minutes in a desiccator (without drying agent), and weighed. The product uniformly lost 1.5-2 mg each hour. Analysis for C and H before and after drying gave the same results (Table 1).

TABLE 1

Elementary Analysis Results Obtained for the Substances After Drying

Name of compound	C (%)		H (%)	
	found	calculated	found	calculated
Naphthalic acid	66.58, 66.69	66.66	4.25, 4.09	4.44
Naphthalic anhydride	72.69, 72.59	72.72	3.16, 3.20	3.03
4,5-Dichloronaphthalic anhydride	53.83, 53.78	53.93	1.7 , 1.62	1.5

TABLE 2

Conversion of Naphthalic Acids into Anhydrides (Time of Drying 7-8 Days, Temperature 27-30°, Amount of Acid 0.05 Mole)

Names of acids	Conversion into anhydride (in %)
4,5-Dichloronaphthalic	100
4,5-Dinitronaphthalic	50
4-Chloronaphthalic	45
4-Nitronaphthalic	15
Naphthalic	10

TABLE 3

Reaction of Naphthalic Anhydride with Aqueous Ammonia

Expt. No.	Amount of taken aqueous ammonia (in ml)	NH_4 concentration (in %)	Duration of heating (in hours)	Amount of recovered naphthalic anhydride (in g)	Yield of imide (in %)	
					on taken anhydride	on reacted anhydride
1	100	6	5.5	–	97.5	–
2	70	6	4.75	0.5	93.5	98.0
3	120	3	5	0.5	95.0	100.0
4	150	4	8	0.16	95.4	96.5
5	500	4.1	6.33	3.87	93.2	99.3
6	775	0.7	8	6.0	85.0	96.6
7	see Expt. 3		13	0.6	77.0	–
8	" "		16	1.25	77.3	–
9	16	7	1	0.27	95.0	97.4

Remarks. 1) In Expts. 1-4 and 7-9 the naphthalic anhydride was taken in 10 g amounts, in Expt. 5 – 59 g, and in Expt. 6 – 50 g. 2) Experiments 7 and 8 were run at the boiling temperature of the solution, 9 – in an autoclave at 170°, and all of the other experiments were run with heating on the boiling water bath. 3) In Expts. 7 and 8, 10 g of NH_4Cl was substituted for the ammonia, while the naphthalic anhydride was first dissolved in 4 g of sodium hydroxide and 150 ml of water.

The substituted naphthalic acids were obtained in the same manner as naphthalic acid. The moist acids were dried at room temperature (27-30°) and weighed each day. The time of drying was 7-8 days. The degree of acid conversion into anhydride was calculated from the elementary analysis results. The rate of conversion is shown in Table 2.

During the next 5 months the 4,5-dichloronaphthalic acid failed to change in weight, the 4,5-dinitro- and 4-chloronaphthalic acids were completely converted into their respective anhydrides, and the 4-nitronaphthalic and naphthalic acids showed approximately 80% conversion into their respective anhydrides. The last two acids were then dried in a thermostat at 99-100°. The nitronaphthalic acid was completely converted into the anhydride in 2 hours, and the napthalic acid in 4 hours.

Naphthalimide. Into a two-necked flask, fitted with stirrer and reflux condenser, was charged 10 g of naphthalic anhydride and ammonia solution of known concentration. The flask was heated on the boiling water bath for 2-8 hours. The precipitate was filtered and treated on the water bath with a 10-fold amount of 3% soda solution. The naphthalimide was filtered, washed with water and dried at 105°. Acidification of the ammoniacal filtrate gave 1-5% of unreacted naphthalic anhydride. The experiments under pressure were run in a glass receptacle, which was contained in a steel autoclave. The results of some of our experiments are shown in Table 3.

SUMMARY

1. The conditions for the conversion of naphthalic acids into anhydrides were studied.

2. Naphthalic acid, free of moisture and anhydride, can be obtained at 15-17°. At 100° naphthalic acid is completely converted into the anhydride.

3. All of the substituted naphthalic acids studied by us were converted into their respective anhydrides more rapidly than is naphthalic acid. Based on their rate of transition into anhydrides, the acids studied by us can be arranged in the following order of decreasing rate: 4,5-dichloronaphthalic, 4,5-dinitronaphthalic, 4-chloronaphthalic, 4-nitronaphthalic, naphthalic.

4. Under direct heating of naphthalic anhydride with aqueous ammonia the anhydride is quantitatively converted into the imide, both at elevated and at atmospheric pressure. The method of Jaeger requires a longer time and gives poorer yields.

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ALKYLAMINO ALKYL ESTERS OF 1-AMINO AND 4-AMINO-5,6,7,8-TETRAHYDRO-2-NAPHTHALENECARBOXYLIC ACIDS

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In association with previous communications [1] we describe in this paper some alkylaminoalkyl esters of the 1-amino- and 4-amino-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acids. These compounds were obtained by the catalytic hydrogenation of the hydrochlorides of the corresponding alkylaminoalkyl esters of the 1- and 4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acids in the presence of skeletal nickel catalyst (taken in an amount equal to the weight of the ester). In this way we prepared the hydrochlorides of the β-diethylaminoethyl, β-dimethylaminoethyl and γ-diethylaminopropyl esters of 1-amino-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid and the hydrochlorides of the β-diethylaminoethyl and β-dimethylaminoethyl esters of 4-amino-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid. The hydrochlorides of the alkylaminoalkyl esters of the 1- and 4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acids were prepared by the reaction of the acid chlorides of the respective nitro acids with equivalent amounts of the dialkylaminoethanols; an exception is the hydrochloride of the γ-diethylaminopropyl ester of 1-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid, which was obtained by the reaction of the acid with an equivalent amount of diethylaminopropyl chloride. The hydrochlorides of the indicated alkylaminoalkyl esters of the 1- and 4-amino-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acids are crystalline substances; their water solutions show slightly alkaline to litmus. Also prepared was the 4-amino-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid derivative in which the dialkylaminoalkyl radical is substituted not on the hydrogen of the carboxyl group, but instead on the hydrogen of the amino group, which derivative was prepared by reacting the ethyl ester of the acid with an equivalent amount of diethylaminoethyl chloride. A water solution of the hydrochloride of this compound shows acid to litmus.

EXPERIMENTAL

The following conditions were used to prepare the hydrochlorides of the β-diethyl and β-dimethylaminoethyl esters of the 1-nitro- and 4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acids: to a solution of the acid chloride of the proper nitro acid in benzene was gradually added under stirring an equivalent amount of the dialkylaminoethanol, after which the stirring was continued for some time under benzene boil; the hydrochloride of the alkylaminoalkyl ester separating here was filtered, washed with benzene and recrystallized.

β-Diethylaminoethyl 1-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). From 7.2 g of the acid chloride the yield was 9.4 g (87%). Colorless substance, crystallizes from a mixture of benzene and anhydrous ethyl alcohol, m.p. 172-173°, readily soluble in anhydrous alcohol, and insoluble in benzene and ether.

Found %: N 7.76. $C_{17}H_{25}O_4N_2Cl$. Calculated %: N 7.85.

β-Dimethylaminoethyl 1-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). The yield from 9.8 g of the acid chloride was 9.6 g (71.6%). Colorless substance, crystallizes from a mixture of methyl alcohol and ethyl acetate, m.p. 167-168°, soluble in chloroform, dichloroethane, methyl, ethyl and isopropyl alcohols, and insoluble in acetone, ethyl acetate and benzene.

Found %: C 54.60; H 6.33; N 8.42. $C_{15}H_{21}O_4N_2Cl$. Calculated %: C 54.82; H 6.44; N 8.52.

β-Diethylaminoethyl 4-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). The yield from 7.2 g of the acid chloride was 5.35 g (50%). Colorless substance, crystallizes from a mixture of ethyl

acetate and ethyl alcohol (4:1), m.p. 170-172°, soluble in ethyl alcohol, and insoluble in ether and ethyl acetate.

Found %: C 57.44; H 7.08; N 7.74. $C_{17}H_{25}O_4N_2Cl$. Calculated %: C 57.21; H 7.06; N 7.85.

β-Dimethylaminoethyl 4-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). From 4.65 g of the acid chloride the yield was 3.1 g (50%). Colorless substance, crystallizes from a mixture of benzene and anhydrous ethyl alcohol, m.p. 181-182°, soluble in acetone and ethyl alcohol, and insoluble in benzene.

Found %: N 8.29. $C_{15}H_{21}O_4N_2Cl$. Calculated %: N 8.52.

γ-Diethylaminopropyl 1-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). A solution of 22.1 g of the acid was prepared by heating in 100 ml of isopropyl alcohol and to it, under stirring, was gradually added 15 g of diethylaminopropyl chloride, the mixture heated at a bath temperature of 85-90° and with stirring for 1 hour, the isopropyl alcohol distilled off, the oily residue vacuum dried and then stirred with ethyl acetate; the precipitate obtained here was filtered and washed with ethyl acetate. Yield 14.7 g (39.6%). Almost colorless substance after recrystallization from a mixture of isopropyl alcohol and ethyl acetate, m.p. 161-163°; soluble in chloroform, methyl alcohol and ethyl alcohol, difficultly soluble in acetone, ethyl acetate and benzene, and insoluble in ether and petroleum ether.

Found %: C 58.19, 58.18; H 7.20, 7.53; N 7.80, 7.67. $C_{18}H_{27}O_4N_2Cl$. Calculated %: C 58.29; H 7.34; N 7.55.

β-Diethylaminoethyl 1-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). A solution was prepared by dissolving 7.5 g of the ester hydrochloride of the 1-nitro acid in 300 ml of anhydrous ethyl alcohol, 7.5 g of skeletal nickel catalyst was added, and the mixture was shaken in a hydrogen atmosphere at atmospheric pressure and with slight warming. On conclusion of reaction the catalyst was removed, the alcohol vacuum distilled, the residue washed with benzene, and then recrystallized several times from a mixture of anhydrous alcohol and benzene. Colorless substance, m.p. 186-187°; soluble in anhydrous ethyl alcohol, and insoluble in ether and petroleum ether.

Found %: C 62.57, 62.60; H 8.27, 8.34; N 8.55. $C_{17}H_{27}O_2N_2Cl$. Calculated %: C 62.46; H 8.33; N 8.57.

β-Dimethylaminoethyl 1-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). Six grams of the ester hydrochloride of the 1-nitro acid was hydrogenated in 450 ml of anhydrous ethyl alcohol at a hydrogen pressure of 10 atm. and 35-40°. After separating the catalyst and distilling off the alcohol in vacuo the oily residue was stirred with ethyl acetate. The white powder obtained here was dissolved at room temperature in dichloroethane, and then the dichloroethane was vacuum distilled. Colorless substance, m.p. 156-157°; readily soluble in methyl, ethyl and isopropyl alcohols, soluble in dichloroethane, and insoluble in ether. Soluble in distilled water in the ratio of approximately 1:5.

Found %: C 60.15; H 7.96; N 9.12. $C_{15}H_{23}O_2N_2Cl$. Calculated %: C 60.29; H 7.76; N 9.35.

β-Diethylaminoethyl 4-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). Five grams of the ester hydrochloride of the 4-nitro acid was hydrogenated in 175 ml of ethyl alcohol at atmospheric pressure for 4 hours. The substance was recrystallized from a mixture of ethyl acetate and anhydrous alcohol. Colorless substance, m.p. 154-155°; readily soluble in methyl and ethyl alcohols, less soluble in acetone, difficultly soluble in boiling dichloroethane, and insoluble in ethyl acetate and benzene. Soluble in water in the ratio of approximately 1:5.

Found %: N 8.45. $C_{17}H_{27}O_2N_2Cl$. Calculated %: N 8.57.

β-Dimethylaminoethyl 4-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). The ester hydrochloride (3.3 g) of the 4-nitro acid was hydrogenated in 150 ml of anhydrous ethyl alcohol at atmospheric pressure and with slight warming for 8 hours. A colorless substance was obtained after repeated recrystallization from a mixture of ethyl acetate and ethyl alcohol, m.p. 195-196°; soluble in methyl and ethyl alcohols, and insoluble in acetone and dichloroethane. Soluble in water in the ratio of approximately 1:5.

Found %: N 9.33. $C_{15}H_{23}O_2N_2Cl$. Calculated %: N 9.35.

γ-Diethylaminopropyl 1-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride). Twelve grams of the ester hydrochloride of the 1-nitro acid was hydrogenated in 180 ml of anhydrous ethyl alcohol

at atmospheric pressure and with slight warming. The obtained substance was stirred with ethyl acetate, the resulting precipitate washed with ethyl acetate, and then recrystallized twice from a mixture of isopropyl alcohol and ethyl acetate (1:10). Nearly colorless needles, m.p. 124° (with decomp.), the substance is readily soluble in dichloroethane and methyl, ethyl and isopropyl alcohols, difficultly soluble in boiling benzene and ethyl acetate, and insoluble in ether. Soluble in water in the ratio of approximately 1:5.

Found %: C 63.38; H 8.55; N 8.25. $C_{18}H_{29}O_2N_2Cl$. Calculated %: C 63.41; H 8.57; N 8.22.

Ethyl N-β-Diethylaminoethyl-4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylate (Hydrochloride) $(C_2H_5)_2N(CH_2)_2HN-C_{10}H_{10}-COOC_2H_5$. To a solution of 1 g of ethyl 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylate in 1.5 ml of benzene was gradually added with stirring a solution of 0.65 g of diethylaminoethyl chloride in 1.3 g of benzene, after which the mixture was heated at the boil and with stirring for 5 hours. The benzene was vacuum-distilled, the residue stirred with petroleum ether, the precipitate obtained here washed with petroleum ether, dissolved in water, aqueous ammonia solution added, the mixture extracted with ether, the ether solution washed with water, dried over sodium sulfate, the ether distilled off, and the residue heated on the water bath at 80° and 10 mm pressure to remove any unreacted diethylaminoethyl chloride. The obtained residue was dissolved in ether and to the ether solution under cooling and with stirring was added an ether solution of hydrogen chloride. The resulting precipitate was filtered, washed with ether until no longer showing acid to Congo, and then recrystallized from a mixture of benzene and petroleum ether. Colorless substance, m.p. 162-164°; soluble in ethyl alcohol and in benzene when heated, and insoluble in petroleum ether. Soluble in water in approximately 1:9 ratio, the water solution showing acid reaction (to litmus).

Found %: N 7.93, 7.88. $C_{19}H_{31}O_2N_2Cl$. Calculated %: N 7.89.

SUMMARY

The alkylaminoalkyl esters of the 1-amino and 4-amino-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acids and the ethyl ester of 4-diethylaminoethylamino-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid were prepared.

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THE PREPARATION OF 4-NITRO-5,6,7,8-TETRAHYDRO-2-NAPHTHALENECARBOXYLIC ACID

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The nitration of 5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid gives 4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid in very low yield [1]. In the present study this nitro acid was synthesized by the nitration of 1-acetamido-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid [2], saponification of the nitro-acetamido acid obtained here, and subsequent deamination of the resulting nitroamino acid. Thus, it was established that in the nitration of 1-acetamido-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid the nitro group enters at the 4 position, as was to be expected on the basis of the results obtained in the nitration of ar-α-acetamidotetrahydronaphthalene [3] and ar-tetrahydro-2-naphthalenecarboxylic acid.

EXPERIMENTAL

1-Acetamido-4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic Acid. To a solution of 49.3 g of 1-acetamido-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid in 165 ml of concentrated sulfuric acid was added with stirring in 30 minutes a solution of 23 ml of 45% nitric acid and 38 ml of concentrated sulfuric acid, maintaining the temperature at −5 to 0°. After all of the mixed acid had been added the mixture was stirred for another 30 minutes at the same temperature, then the reaction mixture was poured into water, the obtained precipitate filtered, and then recrystallized from ethyl alcohol. Yield 39.4 g (67%).

1-Acetamido-4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic Acid was obtained as yellow needles, m.p. 210-211°; soluble when heated in acetone and methyl alcohol, difficultly soluble in ethyl acetate, and insoluble in petroleum ether.

Found %: C 56.43, 56.16; H 4.91, 4.94; N 9.93, 10.05. $C_{13}H_{14}O_5N_2$. Calculated %: C 56.11; H 5.07; N 10.07.

1-Amino-4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic Acid. To a solution prepared by dissolving 5.1 g of sodium hydroxide in 40 ml of hot ethyl alcohol was added 15 g of 1-acetamido-4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid, the mixture boiled for 9 hours, the resulting yellow precipitate filtered, and then thoroughly stirred with 250 ml of water to dissolve any unreacted sodium salt of the original acetamido acid. The sodium salt of the aminonitro acid obtained in this manner (yield 10 g, 72%) was used without further purification for the preparation of 4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid.

One gram of the salt was dissolved in hot water and acidified until showing slightly acid to litmus, the resulting precipitate was filtered, and then recrystallized twice from ethyl alcohol. 1-Amino-4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid was obtained as bright yellow needles; when introduced in a capillary into the melting point apparatus, previously heated to 225°, and with a temperature rise of 5° per minute, the decomposition point was 262°; the substance is difficultly soluble in boiling ethyl alcohol and even more so in the other ordinary organic solvents.

Found %: C 55.93; H 5.02; N 11.61. $C_{11}H_{12}O_4N_2$. Calculated %: C 55.92; H 5.12; N 11.86.

4-Nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic Acid. A suspension, prepared by adding 19.5 g of the sodium salt of 1-amino-4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid to 86 ml of glacial acetic acid, was added in 30 minutes with stirring to a solution of sodium nitrite in 45 ml of concentrated sulfuric acid, mainitaining the temperature not to exceed + 15°. After all of the suspension had been added the stirring was continued at the same temperature for another 30 minutes after which the reaction liquid was

poured in 30 minutes into a vigorously stirred suspension of 21 g of finely powdered cuprous oxide in 180 ml of anhydrous ethyl alcohol, here the temperature rose to 55°. The precipitate was filtered, the filtrate was poured into water, and the precipitate obtained here was filtered. The yield of nitro acid with m.p. 195° was 6.2 g (37.4%). After several recrystallizations from methyl alcohol, m.p. 199°; its mixed melting point with 4-nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid failed to be depressed.

SUMMARY

1. The nitration of 1-acetamido-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid gave 4-nitro-1-acetamido-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid.

2. 4-Nitro-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid was obtained from 4-nitro-1-acetamido-5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid via the saponification and deamination of the latter.

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SYNTHESIS OF SOME N-2,4,5-TRICHLOROPHENOXYACETYLAMINO ACIDS

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The synthesis of N-2,4-dichlorophenoxyacetylamino acids was recently described in the literature [1], being obtained by the reaction of 2,4-dichlorophenoxyacetyl chloride with the corresponding amino acids in the presence of alkalies or pyridine:

$$2,4\text{-}Cl_2C_6H_3OCH_2COCl + RNHCH_2COOH \xrightarrow[\text{or pyridine}]{NaOH}$$

$$\longrightarrow 2,4\text{-}Cl_2C_6H_3OCH_2CON(R)CH_2COOH + NaCl + H_2O.$$

A study of this group of compounds on plants showed that the different optical isomers possess different activity. The presence of different physiological activity for the optical isomers of the 2,4-dichlorophenoxyacetylamino acids gives some basis to assume that their participation in growth metabolism is possible, and in that way shows the possibility for reaction of the halophenoxyacetic acids and their homologs and analogs, when used as plant-growth stimulants and as herbicides, with the amino acids and their transformation products found in plants.

For the purpose of studying the physiologocal activity and to accumulate material on the action mechanism of various compounds we synthesized a number of previously unknown N-2,4,5-trichlorophenoxyacetylamino acids. All of our N-2,4,5-trichlorophenoxyacetylamino acids were synthesized by the reaction of 2,4,5-trichlorophenoxyacetyl chloride with the proper amino acids in the presence of sodium hydroxide. The compounds obtained by us and their properties are given in the table. The methyl ester of N,O-bis(2,4,5-trichlorophenoxyacetyl) tyrosine was synthesized in similar manner, but the reaction was run in the presence of pyridine.

EXPERIMENTAL

Preparation of N-2,4,5-Trichlorophenoxyacetylamino Acids. To a solution of the amino acid in 3 moles of 0.5 N sodium hydroxide solution, cooled to 5°, with good stirring was added dropwise in 10-15 minutes a solution of 1 mole of 2,4,5-trichlorophenoxyacetyl chloride [1] in benzene. After all of the solution had been added the ice was removed, and the mixture was stirred for 2 hours. The obtained precipitate was dissolved in sufficient water, and the solution was extracted with ether (20 ml). The water solution was acidified with hydrochloric acid (1 : 2) until it showed acid to Congo. The obtained precipitate of the 2,4,5-trichlorophenoxyacetylamino acid was filtered, washed with water, dried, and recrystallized.

N,O-Bis(2,4,5-trichlorophenoxyacetyl)-dl-tyrosine Methyl Ester. The methyl ester hydrochloride of dl-tyrosine was obtained by the method of Fischer and Schrauth [2]. A mixture of 4.00 g of the dl-tyrosine methyl ester hydrochloride and 100 ml of dry chloroform was cooled with ice, and to it was added a mixture of 25 ml of pyridine and 50 ml of chloroform. To this mixture with stirring was added dropwise a solution of 9.45 g of 2,4,5-trichlorophenoxyacetyl chloride in 60 ml of chloroform. On conclusion of adding the acid chloride solution the mixture was stirred at room temperature for 5 hours; here the precipitate of the tyrosine methyl ester salt goes into solution at the start. The next day the precipitate of pyridine hydrochloride was filtered, and the filtrate was washed with 10% hydrochloric acid (twice with 250 ml portions of acid) and then with water (100 ml). The chloroform solution was dried over magnesium sulfate, and the solvent was distilled off. After standing for a week in the refrigerator the oily residue crystallized. Yield 10.2 g (88.0%). This

TABLE

N-2,4,5-Trichlorophenoxyacetylamino Acids and Their Properties

Compounds X-2,4,5-$Cl_3C_6H_2OCH_2CO$	Starting substances		NaOH	Benz-	Yield	Solvent for re-	Melting	$[\alpha]_D^{20}$	Analysis for nitrogen (%)	
	Amino acid (moles)	2,4,5-Tri-chloro-phenoxy-acetyl chloride (moles)	0.5 N (ml)	ene (ml)	(in %)	crystallization	point		found	calculated
N-2,4,5-Trichlorophenoxyacetyl-dl-alanine XNHCH(CH_3)COOH	0.025	0.025	150	30	80.8	Dioxane	206*		4.37, 4.43	4.29
N-2,4,5-Trichlorophenoxyacetyl-β-amino-propionic acid XNHCH$_2$CHCOOH	0.0112	0.0112	68	20	82.0	Isopropyl alcohol, dioxane	172		4.45, 4.49	4.29
N-2,4,5-Trichlorophenoxyacetyl-l-leucine XNHCHCOOH $CH_2CH(CH_3)_2$	0.0074	0.0074	44	20	91.6	Dichloroethane, gasoline mixture (b.p. 100-125°)	154-155	−5.8	4.00, 4.00	3.00
N,N-Bis(2,4,5-trichlorophenoxyacetyl)-l-lysine XNHCH$_2$CH$_2$CH$_2$CHCOOH XNH	0.00684	0.01368	68	20	91.7	Dioxane	159-160	−11.2	4.70, 4.63	4.51
N-2,4,5-Trichlorophenoxyacetyl-dl-serine XNHCH(CH_2OH)COOH	0.01	0.01	60	30	69.0	Dioxane	157-158		4.21, 4.28	4.09
N-2,4,5-Trichlorophenoxyacetyl-dl-phenyl-alanine XNHCH($CH_2C_6H_5$)COOH	0.00575	0.00575	34	15	86.2	Dioxane-dichloro-ethane mixture	200		3.41, 3.38	3.48
N-2,4,5-Trichlorophenoxyacetyl-dl-aspartic acid XNHCH(COOH)CH$_2$COOH	0.025	0.025	150	30	69.2	Dioxane-gasoline mixture and chloro-form-acetone mixture	167-169		3.86, 3.79	3.78
N-2,4,5-Trichlorophenoxyacetyl-d-glutamic acid XNHCH(COOH)CH$_2$CH$_2$COOH	0.0117	0.0117	94	15	66.7	Benzene	119-120	+10.6	3.52, 3.60	3.64
N-2,4,5-Trichlorophenoxyacetyl-l-glutamic acid XNHCH(COOH)CH$_2$CH$_2$COOH	0.025	0.025	150	30	76.0	Dioxane, benzene-acetone mixture	119-120	−10.5	3.55, 3.48	3.64
N-2,4,5-Trichlorophenoxyacetyl-dl-glutamic acid XNHCH(COOH)CH$_2$CH$_2$COOH	0.0066	0.0066	40	10	45.4	Benzene-acetone mixture	127.5	−42.9	3.75, 3.69	3.64
N,N'-Bis(2,4,5-trichlorophenoxyacetyl)-l-cystine [(XNHCH)COOH(CH$_2$)$_2$S]	0.01644	0.03288	200	60	76.5	Dioxane-dichloro-ethane mixture, chloroform	141		3.85, 3.82	3.92
N-2,4,5-Trichlorophenoxyacetyl-dl-methion-ine XNHCH(COOH)CH$_2$CH$_2$SCH$_3$	0.067	0.067	40	20	88.0	Dioxane	123-124		3.87, 3.75	3.62
N,S-Bis(2,4,5-trichlorophenoxyacetyl)-dl-cysteine XSCH$_2$CH(COOH)NHX	0.02	0.02	200	50	96.5	Chloroform	146		2.42, 2.48	2.35
N-2,4,5-Trichlorophenoxyacetyl-dl-trypto-phan XNHCH(COOH)CH$_2$C$_8$H$_6$N	0.00392	0.00392	22	10	94.1	Dioxane-dichloro-ethane mixture	98 with decomp.		24.85*, 24.72*	24.96*

* The Cl content is shown (in %).

substance was dissolved in a boiling mixture of 20 ml gasoline (b.p. 100-125°) and 10 ml of chloroform. On cooling the solution the ester separated as an oil, which crystallized after standing in the refrigerator for 2 weeks. The crystals were filtered, dried, and dissolved in 10 ml of boiling carbon tetrachloride. On cooling the ester again came out as an oil, which slowly crystallized when kept in the refrigerator. Yield 3.2 g. M.p. 120-123°.

Found %: N 2.05, 2.02. $C_{26}H_{19}O_7NCl_8$. Calculated %: N 2.09.

SUMMARY

For the purpose of studying the physiological activity on plants and to accumulate material on the mechanism of the action of herbicides and plant-growth stimulants a number of previously unknown N-2,4,5-trichlorophenoxyacetylamino acids were synthesized.

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ALKANESULFONIC ACIDS

XIII. PROPERTIES OF THE N-ARYLAMIDES OF ALKANESULFONIC ACIDS

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We synthesized a whole series of N-arylamides of alkanesulfonic acids of the general formula RSO_2NHAr. These compounds possess great interest from the viewpoint of their chemical properties. Having the NH—group in their composition, where a labile hydrogen atom is connected to the nitrogen, they, as the result of this, are capable of a multitude of substitution reactions. Thus, the hydrogen of the NH—group can be replaced by metals, halogens and various radicals, as, for example: alkyl, acyl, etc. But such reactions have been studied with extreme inadequacy and for the most part of the amides and N-substituted amides of the aromatic sulfonic acids.

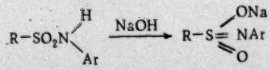
For the alkanesulfonic acids the N-acetyl, N-benzoyl, N-methyl and N-ethyl derivatives of ethanesulfonic acid p-phenetidide are known in the literature [1], and the N-acetylanilides of the vinyl- and ethanesulfonic acids are described briefly [2]; quite recently we described the methylation of a whole series of N-arylamides of alkanesulfonic acids [3]. The salts of the latter were not described, but brief statements exist in the literature on the salts of the aromatic sulfonamides [4]. The chlorination of the amides and N-alkylamides of alkanesulfonic acids leads, as is known from the literature, to N-chloroamides [5]. Nothing is known about the chlorination of the N-arylamides of alkanesulfonic acids. However, relative to the chlorination of the N-arylamides of aromatic sulfonic acids, there is data indicating that their chlorination is neutral medium leads to N-chloroamides, while in either acid or alkaline medium the N-chloroamide rearranges with migration of the halogen into the aromatic nucleus, in which connection the halogen enters at either the para- (in acid medium) or the ortho-position (in alkaline medium) [6] to the sulfoamino group.

The purpose of the present work was to study the chemical behavior of the N-arylamides of alkanesulfonic acids. The subject chosen for study was ethanesulfonamilide taken as being the most typical representative of the mentioned compounds. We studied the reactions for the formation of the salts (sodium and silver) and also their alkylation, the acylation reaction (acetylation, benzoylation and ethosulfonation) and, finally, the chlorination of the ethanesulfonanilide. We prepared the sodium salt of ethanesulfonanilide by the method used to prepare the salt of benzenesulfonamide [4], by which method the treatment of an ether solution of the anilide with the calculated amount of metallic sodium gives as precipitate the completely pure salt in excellent yield. In the absence of moisture the sodium salt is quite stable, and in water it is easily hydrolyzed with the formation of free alkali, which can be easily titrated in the presence of phenolphthalein. As was shown by titration, the salt is hydrolyzed to the extent of 50-70%, both at room temperature and when heated. Its water solution shows pH 8.95. The silver salt of ethanesulfonanilide was obtained from the sodium salt. Both salts are decomposed by dilute acids with the formation of the original ethanesulfonanilide.

The reactions for the formation of the salts, their decomposition by acids, and also the hydrolysis of the sodium salt, can be depicted by the following schemes:

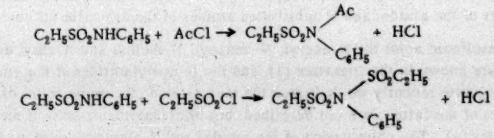
$$RSO_2NHAr + Na \rightarrow RSO_2NNaAr + H,$$
$$RSO_2NNaAr + AgNO_3 \rightarrow RSO_2NAgAr + NaNO_3.$$
$$RSO_2NMeAr + HCl \rightarrow RSO_2NHAr + MeCl.$$
$$RSO_2NNaAr + HOH \rightarrow RSO_2NHAr + NaOH.$$

An attempt to prepare the copper salt of ethanesulfonanilide by the action of an aqueous copper sulfate solution on an aqueous solution of the sodium salt proved unsuccessful. We were also unable to obtain complexes having the composition $(RSO_2NAr)_2Cu \cdot 2ArNH_2$, although analogous complexes were obtained and described by Chugaev for succinimide [7]. It was already mentioned that we had studied the methylation of many alkanesulfonic acid N-arylamides, which methylation takes places with extreme ease in alkaline medium and fails to go at all in organic solvents and in the absence of alkali. The postulation was expressed by us, and also by other authors, that under the influence of alkali the N-arylamides suffer tautomerization in accord with the scheme



But no one has ever isolated such tautomeric forms. To obtain the N- and O-methyl derivatives we had in mind the methylation of the sodium and silver salts of ethanesulfonanilide, similar to the procedure used to obtain them from the sodium and silver derivatives of the carboxylic acid amides [8]. But, as our experiments revealed, in all cases, despite variations in the conditions (in the cold and under heating), the same N-methylethanesulfonanilide with m. p. 65° was obtained, i.e. the methylation product was completely identical with the product that is obtained in the methylation of ethanesulfonanilide itself. Thus, we were unable to isolate the hypothtical tautomeric forms by the technique of methylating the salts, which emphasizes the definite difference that exists in the chemical behavior of the amides of the alkanesulfonic and alkanecarboxylic acids. However, this reaction did reveal that the metal atom on the nitrogen is quite labile and enters into exchange reactions, although it is less active than the hydrogen atom that it displaced.

Included in the other substitution reactions studied by us for ethanesulfonanilide was acylation. The acetylation, benzoylation and ethosulfonation reactions were run with the acid chlorides of the corresponding acids by the scheme.



where: Ac= CH_3CO, C_6H_5CO.

in which connection both the free ethanesulfonanilide and its sodium salt were subjected to acylation.

Our experiments revealed that the acetylation proceeds well if the ethanesulfonanilide or its sodium salt is reacted directly with acetyl chloride under heating on the water bath. The benzoylation proceeds to a somewhat higher temperature (130-160°). The benzoylation product is obtained purer from the salts than it is from the free anilide. If the benzoylation temperature is raised to 200° and higher, then the process is accompanied by cleavage of the ethanesulfonanilide and as a result the anilide of benzoic acid is isolated, having its characteristic melting point. Apparently, the cleavage proceeds in accord with the scheme

$$C_2H_5SO_2NHC_6H_5 + C_6H_5COCl \rightarrow C_2H_5SO_2Cl + C_6H_5CONHC_6H_5.$$

Here the second cleavage product, namely ethanesulfonyl chloride, was not isolated, since at such high temperatures it is completely decomposed. A similar cleavage takes place when acid chlorides of acetic and chloroacetic acid are reacted with substituted amides of arylsulfonic acids [9]; this reaction has not been studied sufficiently, and the cleavage we observed during benzoylation is of definite interest. Apparently, such cleavage also partially exists even at lower temperatures, since the benzoylation of ethanesulfonanilide at 135-160° leads to an impure N-benzoylethanesulfonanilide with low melting point (112-113°, instead of 119-120°). To avoid this reaction we began to run the benzoylation reaction in pyridine at 115-120°. The purest N-benzoylethanesulfonanilide is obtained under these conditions. It should be emphasized that the mentioned compound fails to have a sweet taste, in contrast to the N-benzoylamide of ethanesulfonic acid that was described by us earlier [10].

The ethosulfonation of ethanesulfonanilide was tun in alkaline medium, since the reaction fails to proceed in the absence of alkali. Herein lies an essential difference in the acid chlorides of the sulfonic acids and the acid chlorides of the carboxylic acids, the latter reacting readily with ethanesulfonanilide in the absence of alkali.

The ethosulfonation product N-ethylsulfonylethanesulfonanilide, can also be obtained in the synthesis of ethanesulfonanilide itself: thus, if the reaction of aniline with ethanesulfonyl chloride is run in ether, then only ethanesulfonanilide is formed in accord with the scheme

$$C_2H_5SO_2Cl + 2NH_2C_6H_5 \rightarrow C_2H_5SO_2NHC_6H_5 + C_6H_5NH_2 \cdot HCl. \quad (I)$$

If this same reaction is run in alkaline medium, then a mixture of two products is formed in accord with reactions (I) and (II).

$$2C_2H_5SO_2Cl + NH_2C_6H_5 \rightarrow C_2H_5SO_2N\begin{matrix}C_6H_5\\SO_2C_2H_5\end{matrix} + HCl. \quad (II)$$

The second product is insoluble in alkali, which information was used for separating the mixture.

We thought to obtain the N-chloroamide by the chlorination of ethanesulfonanilide in accord with the scheme

$$C_2H_5SO_2NHC_6H_5 + Cl_2 \rightarrow C_2H_5SO_2NClC_6H_5 + HCl.$$

but instead of the expected product we isolated a quite mobile straw-yellow oil with a specific, but not chloramine, odor. Qualitative analysis of the oil showed the absence of nitrogen and sulfur and the presence of halogen. Quantitative analysis of the oil for halogen and also determination of the molecular refraction, led to the conclusion that the composition of the product corresponds to that of ethyldichlorobenzene $C_2H_5C_6H_3Cl_2$, although the densities for the two fail to agree. The formation of such a product is possible only in the case of profound cleavage for the ethanesulfonanilide molecule, accompanied by rearrangement of the ethyl group into the aromatic nucleus with simultaneous chlorination of the latter. But such a conclusion is not final. It is necessary to make a further study of the composition, properties and structure of the product formed in the chlorination. In any case, on the basis of this observation, it can be concluded that the chlorination of the N-arylamides of the aromatic and alkanesulfonic acids proceeds in entirely different manner.

EXPERIMENTAL

The starting ethanesulfonanilide was synthesized by the method described earlier [11].

Synthesis of Ethanesulfonanilide Salts. Sodium Salt. To a solution of 2 g of ethanesulfonanilide in 10 ml of dry ether was added in small pieces 0.125 g of metallic sodium. After standing for several hours all of the metallic sodium had reacted, and then the white precipitate obtained here was filtered and washed with ether. Yield 1 g (83.3%). The sodium salt of ethanesulfonanilide is a white amorphous powder and decomposes without melting.

Found %: N 6.61; S 14.57. $C_8H_{10}O_2NSNa$. Calculated %: N 6.75; S 15.45.

Silver Salt. To a water solution of 1.65 g of the ethanesulfonanilide sodium salt was added dropwise a 7% water solution of silver nitrate until the separation of a precipitate ceased (25 ml). The precipitate obtained here was filtered rapidly and washed on the filter with alcohol and ether. Yield 2.3 g (74%). The silver salt of ethanesulfonanilide is an amorphous gray powder, quickly darkening in the light, and insoluble in water, alcohol and ether.

Found %: N 4.58; S 10.95; Ag 38.33. $C_8H_{10}O_2NSAg$. Calculated %: N 4.81; S 10.99; Ag 37.07.

Methylation of Ethanesulfonanilide Sodium Salt. To 2 g of a water solution of the salt was added 5 times the calculated amounts of methyl iodide. The rest of the reaction and the isolation of the product were the same as described earlier [3]. The yield of N-methylethanesulfonanilide was 1 g (40%). Lustrous snow-white crystals with m. p. 64-65°.

Found %: N 6.91. $C_9H_{13}O_2NS$. Calculated %: N 7.03.

Methylation of Ethanesulfonanilide Silver Salt. To 0.35 g of ethanesulfonanilide silver salt was added a 5-fold excess of methyl iodide. Considerable self-heating was observed and the reaction mixture foamed. After 1.5 hours the flask contents were treated with alcohol. The insoluble portion (AgI) was filtered, while the alcohol filtrate was precipitated with water under cooling and rubbing with a rod. The precipitate obtained here was filtered and dried. Yield 0.03 g (17%), m. p. 64°.

Found %: N 6.80; S 17.26. $C_9H_{13}O_2NS$. Calculated %: N 7.03; S 16.34.

As a result, the same N-methylethanesulfonanilide is formed in both cases, but better results are observed when the ethanesulfonanilide itself is methylated [3].

Acylation of Ethanesulfonanilide. Acetylation. The ethanesulfonanilide (0.37 g) was treated with 0.18 ml of acetyl chloride (30% excess). A homogeneous yellow liquid was formed. The mixture was heated on the water bath for 3 hours. The mixture gradually thickened during the reaction course. After cooling, the flask contents were transferred to a crystallizing dish. In measure with evaporation of excess acetyl chloride under stirring the product crystallized. The product was purified from alcohol and water. M. p. 108-109°. Yield 0.11 g (79.3%). The acetylation of 0.41 g of ethanesulfonanilide sodium salt with 0.2 ml of acetyl chloride was run in the same

manner. Yield of N-acetylethanesulfonanilide 0.25 g (55.5%), m. p. 108-109°; colorless crystals, soluble in alcohol under heating, and insoluble in water and alkali.

Found %: N 5.91; S 14.16. $C_{10}H_{13}O_3NS$. Calculated %: N 6.17; S 14.09.

Benzoylation. a) A mixture of 0.37 g of ethanesulfonanilide with 0.3 ml of benzoyl chloride (30% excess) was prepared. The reaction was run in pyridine. The mixture was heated in an oil bath at 110-120° for 2 hours. On conclusion of reaction the pyridine was vacuum-distilled, while the residue was transferred to a crystallizing dish. After some standing the mass crystallized. Alcohol and water were used for the purification. M. p. 119-120°. Yield 0.25 g (43.1%). Ethanesulfon-N-benzoylanilide – colorless crystals, insoluble in water and alkali, and soluble in alcohol under heating.

b) The benzoylation of ethanesulfonanilide sodium salt was run under heating in an oil bath at 135-160° for 2 hours. For the benzoylation 0.62 g of ethanesulfonanilide sodium salt was treated with 0.46 ml of benzoyl chloride. The precipitate obtained from the reaction was a mixture of the reaction product and NaCl. Recrystallization from alcohol and water gives N-benzoylethanesulfonanilide with m. p. 119-120°.

Found %: N 4.46; S 10.47. $C_{15}H_{15}O_3NS$. Calculated %: N 4.84; S 11.07.

c) The heating of 0.55 g of ethanesulfonanilide and 0.45 ml of benzoyl chloride at 200° for 2 hours gave considerable tarring of the reaction mixture. After cooling, the mixture was extracted with hot alcohol. The tarry impurities were removed from the alcohol solution by filtration, after which the filtrate was precipitated with water. Here a pale yellow precipitate was obtained, which suffered but slight change in color even after repeated recrystallization from alcohol and water in the presence of activated carbon. The product yield was 0.9 g; m. p. 160°, soluble in CCl_4 under heating, and in alcohol. The qualitative test for sulfur and halogen was negative, while for nitrogen it was positive.

The analysis of the product and its melting point show that the anilide of benzoic acid is formed at an elevated reaction temperature.

Found %: N 6.87. $C_{13}H_{11}ON$. Calculated %: N 7.10.

d) When the reaction is run with the same quantities of ethanesulfonanilide and benzoyl chloride at a lower temperature (136-160°) the product that is formed has m. p. 111-113° instead of 119-120° (m. p. for the pure N-benzoylethanesulfonanilide). This suggests that, apparently, there is partial cleavage of the ethanesulfonanilide with the formation of benzanilide even at lower temperatures; its presence as impurity is the reason for the lower melting point of the N-benzoylethanesulfonanilide.

e) Ethosulfonation. A solution of 0.55 g of ethanesulfonanilide in 8% NaOH solution was prepared and to the alkaline solution was added 0.38 g of ethanesulfonyl chloride. The reaction mixture was heated for 5 hours on the water bath. Toward the end of reaction a yellow oil was obtained, which crystallized on cooling. The precipitate was separated, washed with alkali, and then with water. It was recrystallized from alcohol and water, m. p. 129-130°. The yield of N-ethylsulfonylethanesulfonanilide was 0.21 g (25.4%).

The ethosulfonation of the ethanesulfonanilide sodium salt was run both in the presence and in the absence of water. In the first case the reaction was run in the same manner as described above. From 0.62 g of the salt and 0.38 g of ethanesulfonyl chloride was isolated 0.16 g of N-ethylsulfonylethanesulfonanilide, which is a 19.2% yield, m. p. 129°. The reaction without water was run by mixing 0.621 g of the sodium salt with 0.385 g of ethanesulfonyl chloride. Considerable self-heating and foaming of the reaction mixture was observed. Then the mixture was heated on the water bath for 3 hours. The dry precipitate after reaction was treated with water to dissolve the sodium chloride formed in the reaction. The residue not dissolving in water was recrystallized from alcohol and water, m. p. 129-130°. Yield 0.43 g (52.4%). N-ethylsulfonylethanesulfonanilide was also obtained directly from aniline and ethanesulfonyl chloride. To 2.15 g of aniline was added 3 g of ethanesulfonyl chloride and 15 ml of 7% alkali. The mixture was heated on the water bath for 2.5 hours. The oil settling on the bottom of the flask was separated and transferred to a crystallizing dish. The oil crystallized after a day, m. p. 125-126°. Yield 2.2 g. Since during the reaction course the reaction medium changed from alkaline to neutral we assumed that the crystals obtained here were a mixture of two products: ethanesulfonanilide and N-ethylsulfonylethanesulfonanilide both of which are insoluble in neutral medium. To separate the mixture the precipitate was treated with dilute alkali. Here the ethanesulfonanilide dissolved and was isolated from the alkaline solution by acidification: m. p. 55-56°. The alkali-insoluble N-ethylsulfonylethanesulfonanilide was recrystallized from alcohol and water: m. p. 129°. Yield 0.9 g.

Found %: N 5.17; S 23.17. $C_{10}H_{15}O_4NS_2$. Calculated %: N 5.05; S 23.10.

Chlorination. A vigorous stream of chlorine was passed into a suspension of 4 g of ethanesulfonanilide in 100 ml of water at 0-2° for 3 hours. An oil was gradually formed, which emulsified in the water as flocks. A viscid gray mass settled on the bottom of the reaction flask, which after the reaction was separated and dissolved in alkali. Acidification of the alkaline solution gave crystals of unchanged ethanesulfonanilide; the latter after drying melted at 55-56°. The oil was extracted from the aqueous emulsion with ether. The ether extract was washed several times with water and then dried over calcium chloride. The ether was distilled off on the water bath, while the residual oil was vacuum-distilled (5 mm) at 40-60°. Yield 3 g.

d_4^{20} 1.0268, n_D^{20} 1.46, MR_D 46.6; Calc. 45.28. Found %: Cl 40.07. $C_8H_8Cl_2$. Calculated %: Cl 40.57.

SUMMARY

1. It was shown on the example of ethanesulfonanilide that the N-arylamides possess high reactivity; they are capable of salt-formation, and can also be alkylated, acylated, chlorinated, cleaved, etc.

2. The Na and Ag salts of ethanesulfonanilide were prepared and characterized, and their ability to be alkylated and acylated was studied. It was shown that the same methyl derivative is obtained from either ethanesulfonanilide itself or from its Na and Ag salts, which suggests the absence of tautomerism for the salts.

3. The acyl derivatives of ethanesulfonanilide were prepared; their properties and the conditions for their formation were studied. It was established that N-benzoylethanesulfonanilide, in contrast to N-benzoylethanesulfonamide, fails to have a sweet taste.

4. It was shown that there is an essential difference between the acid chlorides of the carboxylic acids and the acid chlorides of the alkanesulfonic acids; the first react directly with ethanesulfonanilide, the second – only in alkaline medium.

5. It was established that benzoylation at elevated temperature leads to cleavage of the ethanesulfonanilide molecule with the formation of the anilide of benzoic acid.

6. It was shown that the chlorination of ethanesulfonanilide gives, instead of the expected N-chloroethanesulfonanilide, a compound whose composition is close to that of ethyldichlorobenzene.

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CONDENSATION OF ALDEHYDES WITH KETONES

II. SYNTHESIS AND THERMAL CLEAVAGE OF 1,5-DIKETONES

M. N. Tilichenko

A new form of the reaction of saturated aliphatic aldehydes with ketones, established by us earlier on the example of condensing formaldehyde with propiophenone [1], is characterized by the formation of 1,5-diketones, and in this way shows essential difference from the aldol-crotono type of reaction that takes place between the given compounds. Consequently, it is expedient to designate this new form of the reaction by the name of diketonic condensation.

The diketonic type of condensation also proceeds with aromatic aldehydes, which was first established by Kostanecki and coworkers [2], and later by other investigators [3, 4], on the example of condensing acetophenone [2, 3] and propiophenone [4] with benzaldehyde and some other aromatic aldehydes.

However, it is only now that the given reaction acquires a general character, when, as the result of our investigations, it is established that the aliphatic aldehydes are also capable of giving 1,5-diketones when they are condensed with ketones. The reaction can be depicted by the scheme (1):

$$2ArCOCH_2R + R'CHO \rightarrow ArCOCH(R)-CH(R')-CHCOAr + H_2O. \quad (1)$$

In the present communication we describe the synthesis of 1,5-diketones, where: R= H, and R' = H (I), CH_3 (II), C_2H_5 (III), iso-C_3H_7 (IV).

We also studied the relationship between he thermal cleavage reaction of 1,5-diketones and the character of R'. For this purpose we took (I), (II), benzaldiacetophenone (V, R' = C_6H_5), p-dimethylaminobenzaldiacetophenone (VI, R' = $(CH_3)_2NC_6H_4$) and methylenedipropiophenone (VII, R' = H, R= CH_3).

Isolated examples are known in the literature [5-9], showing that the 1,5-diketones under heating are capable of cleavage characteristic for them, and specifically: with rupture of the C-C bond in the β-position to the CO group. For the example of the above indicated 1,5-diketones this is depicted by scheme (2):

$$C_6H_5COCH(X)-CH(R')-CHCOC_6H_5 \rightarrow C_6H_5COCH_2(X) + CH(R')=CCOC_6H_5(X) \quad (2)$$

[X= H, for (I), (II), (V) and (VI), and CH_3 for (VII)].

This phenomenon can be regarded as being a peculiar manifestation of the rule that is known as the "double bond rule" [10, 11]; only here, instead of the C= C double bond, the C= O double bond is involved. But it is possible that this is the reaction result of two "crossed" σπ-systems.

However, the influence of various structural elements in the system of the 1,5-diketone molecule on the course of the given reaction has as yet failed to be studied (by anyone).

Our experiments showed that the 1,5-diketones, in which R' = Ar, are cleaved much more easily than the diketones in which R' = Alk or H; thermally the latter are more stable than the former. We should not fail to mention that this phenomenon is in complete accord with the ability shown by aldehydes for condensation. As is known, the ability shown by aldehydes for condensation can be arranged in the following order: CH_2O > AlkCHO > ArCHO [12, 13].

EXPERIMENTAL

1. The 1,5-diketones were synthesized by the method described earlier [1].

The formaldehyde used was the ordinary 34% formalin. The acetophenone, acetaldehyde and propionaldehyde

were commercial products of the Kharkov Chemical Reagents Plant. The isobutyraldehyde was prepared by the oxidation of isobutyl alcohol; its b. p. was 60-61°.

The formaldehyde reacted with acetophenone almost instantly, the reaction of its homologs was somewhat slower. On conclusion of reaction the condensation product from the isobutyraldehyde (IV) partially crystallized from the reaction mixture when it was cooled to room temperature. After the complete removal of excess acetophenone (by steam-distillation) the other condensation products were obtained as sirupy substances, which for the cases of formaldehyde and acetaldehyde were converted into crystalline masses after some standing, and were then easily purified by recrystallization from alcohol. The sirupy condensation product from the propionaldehyde failed to crystallize, and when vacuum-distilled it suffered noticeable decomposition with the cleavage of acetophenone. This product could be purified only through the semicarbazone, using the method described by Weigand [14]. The experimental results are summarized in Table 1.

Methylenediacetophenone is obtained in about 33% yield if the acetophenone is taken in not less than a 12-fold molar excess on the formaldehyde; when it is used in smaller amounts the main products are 1,5-polyketones.

TABLE 1

Characterization of the Obtained 1,5-Diketones*

Exp. Nos.		Melting Point	Molecular Weight		Elementary Composition (%)					
					Found			Calc.		
			Found	Calc.	C	H	N	C	H	N
1	Methylenediacetophenone (I)	67-68°	–	–	–	–	–	–	–	–
2	Ethylidenediacetophenone (II)	72-73	257,270	266	81.17,81.63	6.66,6.69	–	81.20	6.77	–
3	Propylidenediacetophenone (III)	85-86	276,282	280	81.16,81.32	7.18,7.38	–	81.43	7.14	–
4	Isobutylideneacetophenone (IV)	140-141	310,302	294	81.79,82.00	7.97,7.99	–	81.63	7.48	–
5	(I) Dioxime	164-166	–	–	–	–	–	–	–	–
6	(I) Di-2,4-dinitrophenylhydrazone	233 (decomp.)	–	–	–	–	18.44	–	–	18.30
7	(II) Dioxime	166-168	–	–	–	–	9.76	–	–	9.46
8	(II) Disemicarbazone	208-209	–	–	–	–	21.97,22.17	–	–	22.11
9	(III) Disemicarbazone	207-209	–	–	–	–	20.86,21.31	–	–	21.32

* Methylenediacetophenone [15] and its oxime [15, 16] are described in the literature. The other compounds shown in this table are not described in the literature.

The diketones (II), (III) and (IV) are long white rods, and under the microscope are long prismatic rods and parallelepipeds (from alcohol). They are all readily soluble in benzene, more difficultly soluble in alcohol (especially IV), and very slightly soluble in petroleum ether.

The functional derivatives, shown in Table 1, are very easily obtained by the usual methods. However, the isobutylidenediacetophenone under these conditions, as for the diketones (II) and (III) (heating with semicarbazide hydrochloride in pyridine), failed to give a semicarbazone.

2,6-DIPHENYL-4-METHYLPYRIDINE

(With participation by K. S. Bondarenko)

a) The given base is obtained from ethylidenediacetophenone by the Knoevenagel method [6] in 92% yield. Colorless needlelike rods with bevel-cut ends (from alcohol), m. p. 66°. Soluble in all of the ordinary organic solvents and in the mineral acids – hydrochloric, nitric and sulfuric; it gives an azure fluorescence in the last acid.

Found %: C 87.99, 88.46; H 6.28, 6.34; N 6.08, 6.25. M 250, 245. $C_{18}H_{15}N$.
Calculated %: C 88.16; H 6.12; N 5.72. M 245.

b) The same base is also smoothly obtained from the ethylidenediacetophenone dioxime if dry hydrogen chloride is passed for 3.5 hours at 60° into a dry alcohol-benzene solution of the dioxime. The identity of the two products (a and b) is confirmed by the mixed melting point.

The obtained base readily forms salts with mineral acids (Table 2), which are hydrolyzed with extreme ease by water to give back the original base as a precipitate.

TABLE 2

Salts of 2,6-Diphenyl-4-methylpyridine and Their Analysis

Formula	Melting Point	Titration with 0.1 N KOH			External appearance of the crystals
		Weight of salt (in g)	Consumed (ml)	Calculated (ml)	
$C_{18}H_{15}N \cdot HCl$	199-204° (decompn.)*	0.5628	20.2	20.00	Colorless and with a felted appearance (from conc. HCl)
		0.2266	8.1	8.05	
$C_{18}H_{15}N \cdot H_2SO_4$**	169-170	0.1746	10.07	10.12	Short colorless rods (from alcohol)
		0.1904	10.90	11.04	
$C_{18}H_{15}N \cdot HNO_3$	172-174 (decompn.)*	0.2156	7.11	7.04	Light-yellow rods (from alcohol)
		0.2048	6.58	6.64	

* In a sealed capillary.

** Found %: SO_3 23.16. Calculated %: SO_3 23.31.

The Picrate precipitates immediately when hot alcohol solutions of the base and picric acid are poured together. M. p. 183-184.5°.

Found %: N 12.15 12.12. $C_{24}H_{18}O_7N_4$. Calculated %: N 11.81.

The Ferricyanide Salt was prepared by the Fisenberg method [17]. Because of its ease of hydrolysis with water and its insolubility in alcohol it is not safe to attempt the purification of this salt by the recommended methods [17, 18]. After washing three times with water, then the same number of times with alcohol, and finally drying to constant weight in a vacuum-desiccator the product corresponded to the composition $C_{18}H_{15}N \cdot H_4[Fe(CN)_6]$.

Attempts to oxidize the base (with permanganate, potassium dichromate and nitric acid under various conditions) to the earlier described [19] 2,6-diphenylisonicotinic acid proved unsuccessful.

II. THERMAL CLEAVAGE OF 1,5-DIKETONES

(With participation by G. M. Khirn)

The cleavage of the diketones (II), (V) and (VI was run by the "dry" distillation method in vacuo at 40 mm, and that of the diketones (I) and (VII) at atmospheric pressure. The heating was done in an air bath with regulation of the heating rate (rapidly up to 200°, and then very slowly). The distillation results are given in Table 3.

Redistillation of the distillate (from V) gave: 1st fraction 94-96° (18 mm), 6.7 g; 2nd fraction 219-221° (18 mm), 11.5 g. The first fraction was acetophenone (b. p. 199-201°, m. p. 19.5-20°; 2,4-dinitrophenylhydrazone, m. p. 237-238°) and the 2nd fraction was benzalacetophenone (m. p. 57.5-58°); its mixed melting point with authentic benzalacetophenone was not depressed.

The redistillation of 56.6 g of distillate (from II) gave: 15.5 g of acetophenone (b. p. 199-201°), 20.2 g of ethylideneacetophenone (b. p. 107-109° at 8 mm and 129-131° at 20 mm), d_D^{20} 1.0232, n_D^{20} 1.5586, MR_D 46.04; calc. 44.32; EM_D 1.72 [22, 23], 9.7 g of intermediate fraction and 11.3 g of starting ketone (m. p. 72-73°, from alcohol). When condensed by the Michael method [28] the recovered acetophenone and ethylideneacetophenone again combine to give the diketone (II).

The redistillation at atmospheric pressure of the distillate (from I) gave: 1st fraction 195-202°, 2 g, n_D^{20} 1.5338; 2nd fraction 202-210°, 2.3 g, n_D^{20} 1.5345. Residue 1 g. For acetophenone n_D^{20} 1.53418 [24]. Both fractions gave the same 2,4-dinitrophenylhydrazone identical with that obtained from acetophenone. In ice water the substance congeals to a white crystalline mass, melting at about 20°. With the obtained amount of acetophenone the second fragment of the cleaved methylenediacetophenone (I) could only be vinyl phenyl ketone, which because of its great tendency to polymerize [25] is converted for the most part into a tarry product under the given conditions.

The distillate (from VII) smells of propiophenone and attacks the mucous membranes; the latter is characteristic for isopropenyl phenyl ketone [26]. It fails to be separated by distillation. The main product distilled at 85.5-86.5° (4 mm), leaving as residue 4.6 g of the starting ketone (VII). When distilled a second time at atmospheric pressure

TABLE 3

Dry Distillation of 1,5-Diketones

Exp. Nos.	Preparation	Melting Point	Amount of the Preparation (in g)	Decomposition Temperature*	Duration of Distillation** (in hrs.)	Amount of Distillate (in g)	Residue in the Distillation Flask (in g)
1	(V)	85° [7]	20.8	250	0.5	18.9	1.7 (crystalline – benzalacetophenone)
2	(VI)	124-125 [20]	7.0	245	0.25***	1st fraction: 2.1; 2nd fraction: 4.5	0.2 (crystalline – p-dimethylamino-benzalacetophenone)
3	(II)	72-73	62.5	283	10.0	60.6	1.6 (crystalline – starting diketone)
4	(I)	67-68	9.4	325	5.0	5.6	3.5 (black tar, not studied)
5	(VII)	B. p. 207.5-211.5 (2.5 mm) [1]	48.9	315	4.0	40.5	8.1 (starting diketone)

* The temperature of the bath at which the distillate began to come over.

** The duration of distillation indicates the relative cleavage rate of the 1,5-diketones being compared.

*** The 1st fraction came over in this time, proving to be acetophenone (b. p. 200-202°, m. p. 20°); the 2nd fraction, being p-dimethylaminobenzalacetophenone (m. p. 113-114° [21], from alcohol), distilled more slowly and at a higher temperature.

the substance distilled at 215-224° (mostly at 218-220°); here the fractions taken at 3° intervals had the following n_D^{20}: 1st 1.5292, 2nd 1.5320, 3rd 1.5360 (n_D^{20} of propiophenone 1.5270 [27], of isopropenyl phenyl ketone 1.5342 [26], and of the starting diketone 1.5631). The molecular weight of the collected distillate (138, 140) corresponded to the molecular weight of an equimolar mixture of propiophenone (M 134) and isopropenyl phenyl ketone (M 146).

SUMMARY

1. The condensation of formaldehyde and its homologs with acetophenone gave a homologous series of 1,5-diketones with the formula:

$$C_6H_5COCH_2-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2COC_6H_5.$$

To distinguish it from the usual type of aldol-crotono condensation, we have suggested the name of diketonic condensation for this form of reaction shown by aldehydes with ketones.

2. On the example of ethylideneacetophenone it was shown that the given 1,5-diketones can be converted under the influence of hydroxylamine hydrochloride directly on the diketone or under the influence of hydrogen chloride on the diketone oxime into 2,6-diphenyl-4-alkylpyridines. From ethylidenediacetophenone and its dioxime we obtained and characterized 2,6-diphenyl-4-methylpyridine.

3. The thermal cleavage of a number of 1,5-diketones was run under comparable conditions, and specifically: methylene-, ethylidene-, benzylidene- and p-dimethylaminobenzylidene-diacetophenones, and also methylene-dipropiophenone.

4. The enumerated 1,5-diketones are smoothly cleaved in accord with Scheme (2), with rupture of the C–C bond in the β-position to the CO group. The temperature thresholds at which fairly effective cleavage by the given scheme begins were established.

5. It is established that the ease of cleavage of the indicated type of 1,5-diketones essentially depends on the character of the radical (R) in the β-position. The arylidenediketones are cleaved with considerably greater ease than are the alkylidenediketones. Among the latter the diketones with R= H are thermally more stable than are the diketones with R= Alkyl.

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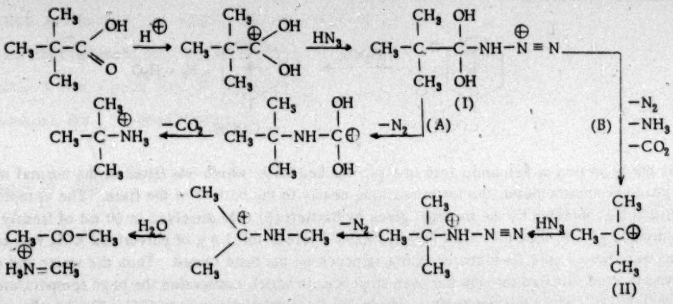
* T. p. = Consultants Bureau Translation pagination.

THE REACTION OF 1-APOCAMPHANECARBOXYLIC ACID WITH HYDRAZOIC ACID

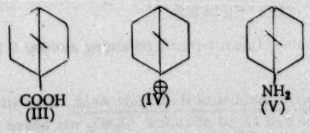
D. N. Kursanov and S. V. Vitt

The reaction of organic compounds with hydrazoic acid in the presence of strong mineral acids, having been given the name of the Schmidt reaction [1], is an effective method for the synthesis of amines and their derivatives and has attracted the attention of investigators [2] for a long time. Recently, Schuerch and Huntress [3, 4] published a communication on the anomalous behavior shown by carboxylic acids containing a tertiary α-carbon atom under the conditions of the Schmidt reaction.

Thus, in studying the reaction of trimethylacetic acid with hydrazoic acid in the presence of sulfuric acid these authors found that together with the normal reaction product – tertbutylamine, which was isolated in 33% yield, the formation of acetone, methylamine and ammonia also takes place. From the schemes postulated for this reaction by the indicated authors and the one given below it follows that the formation of the indicated secondary products is caused by the decomposition of the intermediate cation (I) in direction (B), different from the direction of the normal reaction (A). Here cation (I) is converted into the trimethylcarbonium ion (II), the reaction of which with hydrazoic acid leads to the formation of methylamine and acetone.



It appeared of undoubted interest to study the mechanism of the Schmidt reaction on an acid in which the hydrocarbon radical was incapable of existing as a kinetically independent cation. For this purpose we studied the reaction of hydrazoic acid with 1-apocamphanecarboxylic acid (III).



According to Bartlett [5], the formation of the nonplanar carbonium ion (IV) (corresponding to the hydrocarbon radical of acid III) requires the consumption of a considerably greater amount of energy (by 22 kcal./mole) than is necessary for the formation of ordinary planar carbonium ions. This circumstance should prevent the formation of the carbonium ion in the reaction of acid (III) with hydrazoic acid, and it could be assumed in this case that the secondary reaction (B) would be stopped, and that the direction of the normal reaction (A) – the intramolecular shifting of the apocamphanyl radical from the carbon atom to the nitrogen – would become the solitary direction of the reaction.

Actually, in accord with the above postulations, we found that the product formed exclusively in the reaction of 1-apocamphanecarboxylic acid with hydrazoic acid is 1-apocamphanylamine (V). This substance is formed in extremely high yield, reaching 94%, which is considerably higher than the yields given in the litetature for amines that are obtained by Schmidt reactions from acids containing a tertiary α-carbon atom; here we were completely unable to show the presence of any substances that corresponded to the progress of reaction (B).

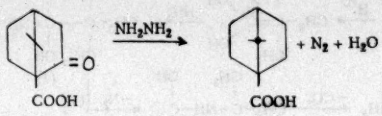
The obtained data led us to the conclusion that the formation of a kinetically independent carbonium ion is not always dependent on the intermediate stage of the Schmidt reaction. It is interesting to compare our conclusion with the earlier noted facts of optical activity retention when the Schmidt reaction is run with compounds containing an asymmetrical α-carbon atom. Thus, for example, Braun [6] observed that optical activity is retained in the reaction for the transformation of optically active methylbenzylacetic acid into 1-phenyl-2-amino-propane.

$$C_6H_5-CH_2-\overset{*}{C}H(CH_3)-COOH \xrightarrow{HN_3} C_6H_5-CH_2-\overset{*}{C}H(CH_3)-NH_2 + N_2 + CO_2.$$

EXPERIMENTAL

1. 1-Apocamphanecarboxylic Acid. According to the literature this acid is obtained either by the Clemmensen reduction of ketopinic acid (in yields up to 60%) [5, 7] or by the heating of ketopinic acid semicarbazone with sodium ethylate in a sealed tube (in yields up to 62% [5, 8].

Below we give the method developed by us for the preparation of 1-apocamphanecarboxylic acid, which method is based on the reaction:



We ran the reduction of ketopinic acid in a two-necked flask, which was fitted in the normal manner with a total reflux head and thermometer, the latter reaching nearly to the bottom of the flask. The ketopinic acid (6.2 g) (m. p. 232.5-233.5°), obtained by the method given by Bartlett [5], was dissolved in 50 ml of freshly vacuum-distilled triethylene glycol; then 6.0 ml of 98% hydrazine hydrate and 7.0 g of pulverized KOH was added. The flask contents were boiled on a flask heater with a stopcock on the head closed. Then the water and excess hydrazine hydrate were distilled through the open stopcock, in which connection the head temperature was maintained at 115-120°, while the temperature inside the flask gradually rose to 195°. The heating at 196-202° was continued for 3.5 hours in which connection the originally vigorous nitrogen evolution had completely ceased by the end. The colorless reaction mixture was cooled, poured into 100 ml of water and then acidified with 20% sulfuric acid. The 1-apocamphanecarboxylic acid separated as fine crystals, which were filtered and washed with water. Recrystallization from 50% ethanol gave 4.75 g of substance with m. p. 217.5-218.5°. From the literature 1-apocamphanecarboxylic acid melts at 217-218°. Yield 83%.

Distillation of the alcohol from the mother liquor permits obtaining another 0.21 g of the acid with m. p. 215-217°.

2. Reaction of 1-Apocamphanecarboxylic Acid with Hydrazoic Acid. To a stirred mixture of 4.2 g of 1-apocamphanecarboxylic acid, 25 ml of benzene and 15 ml of concd. H_2SO_4 was added in 30 minutes at 35-40° 2.28 g of sodium azide. On conclusion of sodium azide addition the mixture was stirred for 1 hour at 50°, cooled, and poured over 50 g of ice. The benzene layer was separated, and the water layer was extracted with benzene (3 times with 20 ml portions). The combined benzene extracts were washed with water, and dried over magnesium sulfate. Removal of the benzene by distillation failed to leave any high-boiling residue.

The acid water layer was made alkaline under ice-cooling with a solution of 35 g of NaOH in 100 ml of water and then it was steam-distilled. The base was extracted from the distillate with n-pentane (3 times with 20 ml portions), and the extract was dried over potash. After distilling off the solvent the residue gave 3.29 g of of 1-apocamphanylamine with m. p. 175-177° (in a closed capillary). Bartlett gives [5] a m. p. of 175°. Yield 94.5%.

N-Acetyl Derivative, m. p. 131-132° (from n-heptane). From the literature [5] N-1-apocamphanylacetamide melts at 132°.

Found %: N 7.52, 7.45. $C_{11}H_{19}ON$. Calculated %: N 7.72.

SUMMARY

1. The Schmidt reaction was studied with 1-apocamphanecarboxylic acid. It was shown that the reaction of 1-apocamphanecarboxylic acid with hydrazoic acid results in the exclusive formation of 1-apocamphanylamine in 94% yield.

2. The mechanism of the reaction was analyzed. The absence in the studied case of secondary products, characteristic for the Schmidt reaction with tertiary acids, is explained by the steric difficulties that are associated with the formation of a nonplanar carbonium ion.

3. A convenient synthesis method for 1-apocamphanecarboxylic acid was developed.

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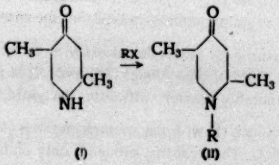
HETEROCYCLIC COMPOUNDS

XXXIV. SYNTHESIS OF 4-PIPERIDONES, 4-PIPERIDINOLS AND THEIR ETHERS, CONTAINING KETOALKYL RADICALS ON THE NITROGEN

I. N. Nazarov and E. M. Cherkasova

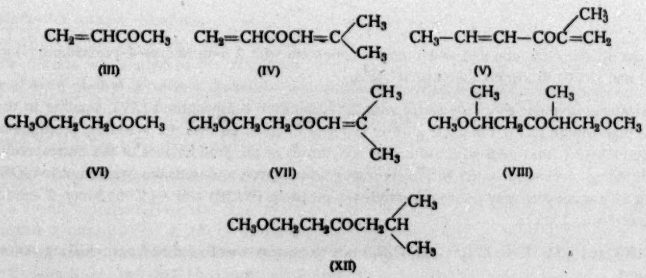
In the preceding communication [1] we described the alkylation of 2,5-dimethyl-4-piperidone (I) to the corresponding 1-alkyl-2,5-dimethyl-4-piperidones (II):



(I) (II)

In expanding these studies it seemed of interest to us to also synthesize the γ-piperidones and the γ-piperidinols and their ethers, all of them showing the presence of a ketoalkyl chain on the nitrogen. Among synthetic substances such compounds have not been described up to now, although a number of related substances with a ketonic side chain in the piperidone nucleus are found among the natural-occurring alkaloids (pelletierine, isopelletierine, lobelanine, etc.).

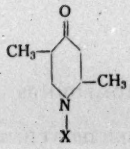
For the designated studies we chose the readily available 2,5-dimethyl-4-piperidone (I) [2], into the molecule of which the ketonic substituents were introduced (on the nitrogen) by three methods: 1) addition of α,β-unsaturated ketones, 2) reaction with β-methoxyketones and 3) reaction with halo-substituted ketones.

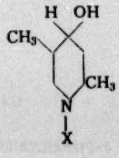


(III) (IV) (V)

(VI) (VII) (VIII)

(XII)





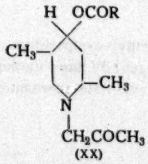
(IX) X=$CH_2CH_2COCH_3$, (X) X=$CH_2CH_2COCH{=}C(CH_3)_2$,
(XI) X=$CH{-}CH_2COC{=}CH_2$, (XIII) X=$CH_2CH_2COCH_2CH(CH_3)_2$,
CH_3 CH_3
(XIV) X=$CHCH_2COCH{-}CH_3$,
CH_3 CH_3
(XVII) X=$CH_2COC_6H_5$, (XXIII) X= , (XXIV) X=$CH_2C(CH_3)C_6H_5$.
O OH

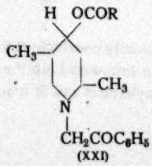
(XV) X=H, (XVIII) X=CH_2COCH_3,
(XIX) X=$CH_2COC_6H_5$.

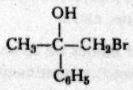
The reaction of 2,5-dimethyl-4-piperidone (I) with the α,β-unsaturated ketones (III, IV, V) gives the corresponding γ-piperidones (IX, X, XI), containing ketonic radicals on the nitrogen.

The addition of 2,5-dimethyl-4-piperidone (I) proceeds easiest with the unsaturated ketones (III) and (IV), both containing an unsubstituted vinyl group (the yield of piperidones (IX) and (X) is about 60%), while the propenyl isopropenyl ketone (V) this reaction proceeds with considerably greater difficulty (the yield of piperidone (XI) is about 30%).

The reaction of 2,5-dimethyl-4-piperidone (I) with the methoxyketones (VI, VII, VIII) also gives the piperidones (IX, X, XI), but in lower yield (15-20%). This reaction proceeds only on heating and in the presence of water, which was already mentioned earlier in previous communications [3]. The hydrogenation of piperidones (X) and (XI) gave the corresponding saturated piperidones (XIII) and XIV). Piperidone (XIII) is also obtained in about 15% yield by heating the methoxyketone (XII) with 2,5-dimethyl-4-piperidone (I) in the presence of water.


(XX)


(XXI)


(XXII)

The reactions of bromoacetone and ω-bromoacetophenone with 2,5-dimethyl-4-piperidone (I) gave the piperidones (XVI) and (XVII) in almost theoretical yield.

The indicated reaction also proceeds easily with 2,5-dimethyl-4-piperidinol (XV), leading to the formation in high yields of the piperidinols (XVIII) and XIX). The latter are converted into the acetates, propionates and benzoates (XX) and XXI) by treatment with either the anhydrides or the acid halides of the corresponding acids. The reaction of 2,5-dimethyl-4-piperidone (I) with α-bromocyclohexanone and with the bromohydrin (XXII) resulted in our also obtaining 1-(α-oxocyclohexyl)-2,5-dimethyl-4-piperidone (XXIII) and 1-(2'-hydroxy-2'-phenylpropyl)-2,5-dimethyl-4-piperidone (XXIV).

The esters (XX and XXI; R = CH_3, C_2H_5, C_6H_5) fail to possess a well-defined pain-killing, anesthetic or spasmolytic action.*

* The pharmacological studies of these compounds were made in the S. Ordzhonikidze All-Union Chemical-Pharmaceutical Institute under the direction of M. D. Mashkovsky.

EXPERIMENTAL*

1-(3'-Oxobutyl)-2,5-dimethyl-4-piperidone (IX). In a round-bottomed flask, fitted with reflux condenser, was placed 5 g of 2,5-dimethyl-4-piperidone (I) with b. p. 61-63° at 5 mm [2], 4.83 g of 1-methoxy-3-butanone (VI) (b. p. 140-141° (750 mm), n_D^{26} 1.0430) and 1.3 ml of water. The mixture was heated for 6.5 hours at 140-150°. Then hydrochloric acid solution (1:1) was added under cooling until the reaction showed acid to Congo, and the unreacted 1-methoxy-3-butanone was extracted with ether. The acid water layer was neutralized with potassium hydroxide, the floating oil extracted several times with ether, the ether extract dried over fused sodium sulfate, and then after distilling off the ether, the residue was vacuum-distilled. The yield of 1-(3'-oxobutyl)-2,5-dimethyl-4-piperidone (IX) was 2 g.

B. p. 111-112° (1.5 mm), n_D^{20} 1.4810, d_4^{20} 1.0760, MR_D 52.16; calc. 52.02.
Found %: N 7.34, 7.22. $C_{11}H_{19}O_2N$. Calculated %: N 7.10.

Methiodide — tiny colorless needles with m. p. 191-192° (from alcohol).

1-(1',4'-Dimethyl-3'-oxo-4'-pentenyl)-2,5-dimethyl-4-piperidone (XI). a) Into a round-bottomed flask was charged 14.6 g of 2,5-dimethyl-4-piperidone (I) and 15 g of propenyl isopropenyl ketone (V) with b. p. 45-48° (11 mm) [3]. The mixture was heated on the water bath at 75-80° for 11 hours, then for 5 hours at 100° and for 1 hour at 120°. The mixture, when worked up in the same manner as described above, gave 9 g of 1-(1',4'-dimethyl-3'-oxo-4'-pentenyl-2,5-dimethyl-4-piperidone (XI).

B. p. 138-139° (1.5 mm), n_D^{20} 1.4850, d_4^{20} 0.9777, MR_D 68.60; calc. 68.14.
Found %: N 6.23, 6.02. $C_{14}H_{23}O_2N$. Calculated %: N 5.91.

Methiodide — tiny colorless needles with m. p. 185-186° (from alcohol).

b) Into a round-bottomed flask was charged 5 g of 2,5-dimethyl-4-piperidone (I), 8.7 g of 1,5-dimethoxy-2-methyl-3-hexanone (VIII) with b. p. 90-91° (11 mm) [3], and 1.7 ml of water. The mixture was heated for 10 hours at 110-115°. After appropriate treatment there was obtained 2.1 g of 1-(1',4'-dimethyl-3'-oxo-4'-pentenyl) 2,5-dimethyl-4-piperidone (XI) with b. p. 144-148° (4 mm), $n_D^{20.5}$ 1.4858.

1-(1',4'-Dimethyl-3'-oxopentyl) 2,5-dimethyl-4-piperidone (XIV). A solution of 4.2 g of the unsaturated piperidone (XI) in 35 ml of ethanol was hydrogenated in the presence of nickel catalyst. The amount of hydrogen absorbed was 440 ml instead of the theoretical 433 ml. The solution was filtered, the alcohol distilled off, and the residue vacuum-distilled. The yield of 1-(1',4'-dimethyl-3'-oxopentyl)-2,5-dimethyl-4-piperidone (XIV) was 1.5 g.

B. p. 111-113° (1.5 mm), n_D^{20} 1.4766, d_4^{20} 0.9815, MR_D 68.78; calc. 68.61.
Found %: N 6.11, 6.08. $C_{14}H_{25}O_2N$. Calculated %: N 5.86.

Methiodide — tiny colorless needles with m. p. 190-190.5° (from alcohol).

1-(5'-Methyl-3'-oxo-4'-hexenyl)-2,5-dimethyl-4-piperidone (X). a) Into a round-bottomed flask was charged 23.7 g of 2,5-dimethyl-4-piperidone (I) and 20.5 g of 1,1-dimethylvinyl vinyl ketone (IV) (b. p. 43-45° (7 mm) [4]). The mixture was heated on the water bath for 8 hours at 65°. After the usual treatment there was obtained 27 g of 1-(5'methyl-3'-oxo-4'-hexenyl)-2,5-dimethyl-4-piperidone (X).

B. p. 134-135° (1.5 mm), n_D^{20} 1.4855, d_4^{20} 0.9997, MR_D 68.93; calc 68.14.
Found %: N 5.81, 5.92. $C_{14}H_{25}O_2N$. Calculated %: N 5.91.

Methiodide — tiny colorless needles with m. p. 184-185° (from alcohol).

b) Into a round-bottomed flask was charged 15 g of 2,5-dimethyl-4-piperidone (I), 18.8 g of 1-methoxy-5-methyl-4-hexen-3-one (VII) (b. p. 75-77° (8 mm)) [5] and 3.5 ml of water. The mixture was heated for 10 hours at 140°. After the usual treatment there was obtained 3.7 g of 1-(5'-methyl-3'-oxo-4'-hexenyl)-2,5-dimethyl-4-piperidone (X) with b. p. 135-137° (1.5 mm), n_D^{20} 1.4850.

1-(5'-Methyl-3'-oxohexyl)-2,5-dimethyl-4-piperidone (XIII). a) Into a round-bottomed flask was charged 12.5 g of 2,5-dimethyl-4-piperidone (I), 15.9 g of β-methoxyethyl isobutyl ketone (XII) (b. p. 72-72.5° (13 mm)) [6] and 3 ml of water. After the usual treatment there was obtained 2.8 g of 1-(5'-methyl-3'-oxohexyl)-2,5-dimethyl-4-piperidone (XIII).

* Student Yu. Segal participated in the experimental portion of this work.

B. p. 125-127° (1.5 mm), n_D^{20} 1.4738. d_4^{20} 0.9761. MR_D 68.82; calc. 68.61.
Found %: N 6.03, 6.23. $C_{14}H_{25}O_2N$. Calculated %: N 5.86.

Methiodide – colorless needles with m. p. 187-188° (from alcohol).

b) A solution of 8.7 g of the unsaturated piperidone (X) in 60 ml of ethanol was hydrogenated in the presence of nickel catalyst at room temperature for 9 hours. The amount of hydrogen absorbed was 1.24 liters instead of the theoretical 1.056 liters. After filtering the solution and distilling off the alcohol the residue was vacuum-distilled. The yield of 1-(5'-methyl-3'-oxohexyl)-2,5-dimethyl-4-piperidone (XIII) with b. p. 123-125° (1.5 mm), n_D^{21} 1.4740, was 6.2 g.

Methiodide – tiny colorless needles with m. p. 187-188° (from alcohol). Its mixed melting point with the preceding specimen failed to be depressed.

1-Acetonyl-2,5-dimethyl-4-piperidone (XVI). In a round-bottomed flask, fitted with reflux condenser, was placed 35.4 g (2 moles) of freshly-distilled 2,5-dimethyl-4-piperidone (I) in a solution of 10 ml of absolute ether. To this solution was added 19.1 g (1 mole) of bromoacetone (obtained by the bromination of acetone [10], b. p. 43-44° (13 mm)), dissolved in 15 ml of absolute ether. Self-heating began soon, the ether boiled, and cooling of the flask was required. Within several minutes a precipitate of the 2,5-dimethyl-4-piperidone hydrobromide began to form. The mixture was allowed to stand overnight, and the next day it was heated on the water bath for 30 minutes. The precipitate (26 g) obtained here was separated, washed several times with absolute ether, and from it after treatment with an aqueous caustic solution there was isolated 15 g of the starting 2,5-dimethyl-4-piperidone (I).

The ether was distilled from the ether solution, the residue was neutralized with 25 ml of dilute hydrochloric acid (1:1), and then it was extracted with ether to remove any unreacted bromoacetone. The water solution was treated with solid caustic, the floating dark oil was extracted several times with ether, and then dried over sodium sulfate. After two distillations there was obtained 18.2 g of 1-acetonyl-2,5-dimethyl-4-piperidone (XVI).

B. p. 105-107° (1 mm), n_D^{20} 1.4760, d_4^{20} 1.0268, MR_D 50.29; calc. 50.14.
Found %: N 7.51, 7.43. $C_{10}H_{17}O_2N$. Calculated %: N 7.65.

The Picrate, obtained by mixing the substance with a saturated alcohol solution of picric acid, melted at 154-155.5° (from alcohol).

Found %: N 13.17, 13.27. $C_{16}H_{20}O_9N_4$ Calculated %: N 13.56.

After distilling off the ether from the neutral products there was obtained 4.5 g of bromoacetone.

1-Acetonyl-2,5-dimethyl-4-piperidone (XVI) was also obtained under similar conditions by reacting chloroacetone with 2,5-dimethyl-4-piperidone (I), but in smaller yield.

1-Phenacyl-2,5-dimethyl-4-piperidone (XVII). A solution of 11.8 g (1 mole) of ω-bromoacetophenone (m. p. 48-49°) in 55 ml of absolute ether was stirred with 15.1 g (2 moles) of freshly-distilled 2,5-dimethyl-4-piperidone (I). A precipitate of the 2,5-dimethyl-4-piperidone hydrobromide began to form within a few minutes. The mixture was allowed to stand overnight after which it was heated for 5 hours on the water bath at ether boil and then it was worked up as described above. From the ether solution of the base after distilling off the ether there was obtained 8 g of 1-phenacyl-2,5-dimethyl-4-piperidone (XVII) as colorless crystals, which after recrystallization from 30% aqueous alcohol melted at 75-76°.

Found %: C 73.44, 73.57; H 7.43, 7.52; N 5.85, 5.95. $C_{15}H_{19}O_2N$. Calculated %: C 73.43; H 7.90; N 5.72.

After ether removal from the neutral products there was obtained 2.3 g of ω-bromoacetophenone.

1-(α-Oxocyclohexyl)-2,5-dimethyl-4-piperidone (XXIII). A solution of 20 g (1 mole) of 2,5-dimethyl-4-piperidone (I) in 25 ml of dioxane was mixed with 31.1 g (1.1 mole) of α-bromocyclohexanone* (b. p. 101-102° (14 mm)) in 25 ml of dioxane. The reaction mass was heated at 130° for 6 hours and the next day it was worked up as described above.

After distilling off the ether there was obtained from the residual base 2 g of 1-(α-oxocyclohexyl)-2,5-dimethyl-4-piperidone (XXIII) as colorless needles which melted at 186-187° (from 30% alcohol).

* α-Bromocyclohexanone was obtained in about 60% yield by the bromination of cyclohexanone with dioxane dibromide and subsequent vacuum-distillation in a nitrogen stream [7].

Found %: N 6.185, 6.19. $C_{13}H_{21}O_2N$. Calculated %: N 6.32.

From the liquid portion of the base after two vacuum-distillations there was obtained 15 g of the starting 2,5-dimethyl-4-piperidone (I) with b. p. 52-60° (5 mm). After distilling off the ether from the neutral products there was obtained 10.2 g of α-bromocyclohexanone.

1-Acetonyl-2,5-dimethyl-4-piperidinol (XVIII). In a flask was placed 12.0 g (1 mole) of 2,5-dimethyl-4-piperidinol (XV) (m. p. 95-96°), obtained by the reduction of piperidone (I) with sodium in alcohol [8], in 50 ml of anhydrous alcohol and 15.1 g (1.1 mole) of bromoacetone. The mixture was let stand overnight and then next day it was heated for 4 hours on the water bath. The resulting precipitate was filtered, repeatedly washed with absolute ether, and dried in a vacuum-desiccator. The yield of 1-acetonyl-2,5-dimethyl-4-piperidinol (XVIII) hydrobromide with m. p. 209-211° was 14.5 g.

Found %: N 5.33, 5.12. $C_{10}H_{20}O_2NBr$. Calculated %: N 5.26.

Treatment of the crystals of this hydrobromide with aqueous caustic solution gave 10.3 g of the free base, 1-acetonyl-2,5-dimethyl-4-piperidinol (XVIII), with b. p. 132-133° (2 mm).

Found %: N 7.45, 7.64. $C_{10}H_{19}O_2N$. Calculated %: N 7.54.

In addition, in this experiment 2 g of the starting 2,5-dimethyl-4-piperidinol (XV) was recovered.

1-Acetonyl-2,5-dimethyl-4-piperidinol Acetate (XX, R= CH_3). For reaction was taken 5.25 g of freshly-distilled 1-acetonyl-2,5-dimethyl-4-piperidinol (XVIII) (b. p. 115-117° (0.5 mm)) and 21 ml of freshly-distilled acetic anhydride, the latter having been previously saturated with dry hydrogen chloride for 30 minutes. The solution turned dark and became homogeneous. The next day the mixture was heated for 4 hours on the water bath. After cooling, the solution was again saturated with dry hydrogen chloride for several minutes. Then the excess acetic anhydride was distilled off under slight vacuum, after which the residue crystallized immediately (8 g). The crystals of 1-acetonyl-2,5-dimethyl-4-piperidinol (XX, R= CH_3) acetate hydrochloride obtained here were purified by 2-fold precipitation from alcohol solution with absolute ether and subsequent washing with acetone, m. p. 194-196°.

Found %: N 5.50, 5.31; Cl 13.57. $C_{12}H_{22}O_3NCl$. Calculated %: N 5.32; Cl 13.46.

1-Acetonyl-2,5-dimethyl-4-piperidinol Propionate (XX, R= C_2H_5). Five grams of freshly-distilled 1-acetonyl-2,5-dimethyl-4-piperidinol (XVIII) (b. p. 139-140° (3 mm)) was mixed with excess propionic anhydride, which had previously been saturated with dry hydrogen chloride for 45 minutes. On shaking the mixture the piperidinol slowly dissolved with considerable heat-evolution. The reaction mass was let stand overnight, after which the excess solvent was vacuum-distilled.

The crystalline residue (7 g) was dissolved in warm anhydrous alcohol and precipitated with absolute ether. This operation was repeated twice. After drying in a vacuum-desiccator the white crystals of 1-acetonyl-2,5-dimethyl-4-piperidinol propionate (XX, R= C_2H_5) hydrochloride obtained here melted at 181.5-183°. The substance is soluble in water.

Found %: C 56.48; 56.68; H 8.76, 8.41; N 5.13, 5.23. $C_{13}H_{24}O_3NCl$. Calculated %: C 56.3; H 8.7; N 5.05.

1-Acetonyl-2,5-dimethyl-4-piperidinol Benzoate (XX, R= C_6H_5). For reaction was taken 10.3 g of 1-acetonyl-2,5-dimethyl-4-piperidinol (XVIII) (b. p. 132-133° (2 mm)) and 44 g of benzoyl chloride, the latter having been previously saturated with dry hydrogen chloride. The next day the mixture was heated for 6 hours at 115-120°. After removing the benzoyl chloride by vacuum-distillation the isolated residue weighed 17 g. Further purification was the same as described in the preceding experiment.

After drying in a vacuum-desiccator the colorless crystals of the 1-acetonyl-2,5-dimethyl-4-piperidinol benzoate (XX, R= C_6H_5) hydrochloride melted at 205-206.5°. The substance is soluble in water.

Found %: C 62.60, 62.40; H 6.97, 6.96; N 4.50, 4.56. $C_{17}H_{24}O_3NCl$. Calculated %: C 62.69; H 7.42; N 4.3.

1-Phenacyl-2,5-dimethyl-4-piperidinol (XIX). In a round-bottomed flask, fitted with reflux condenser, was placed a solution of 9.8 g (1 mole) of 2,5-dimethyl-4-piperidinol (XV) (m. p. 93-94°) in 40 ml of dioxane and 16 g (1.1 moles) of ω-bromoacetophenone in 40 ml of dioxane. The mixture was heated for 4 hours at 110-115° and allowed to stand overnight. The next day the solvent was distilled off under slight vacuum. The residue was

worked up in the usual manner. The residual solution was treated with solid caustic and potash, and the base separating here was repeatedly extracted with ether. The ether extracts were dried over sodium sulfate. After distilling off the ether and unreacted 2,5-dimethyl-4-piperidinol (XV) in vacuo the residual dark oil was dissolved in absolute ether, through which dry hydrogen chloride was passed. The 1-phenacyl-2,5-dimethyl-4-piperidinol (XIX) hydrochloride that separated here was obtained as red, very hygroscopic oily crystals, rapidly decomposing in the air.

We found that completely stable colorless crystals of substance (XIX) could be isolated by the following operations: the oily slurry was heated with dry acetone on the water bath for 1.5 hours. Then the crystalline precipitate, considerably lighter in color, was filtered and repeatedly washed with dry acetone on the filter. After drying in a vacuum-desiccator the 1-phenacyl-2,5-dimethyl-4-piperidinol hydrochloride (8 g) melted at 105-107°.

Found %: N 4.74, 4.72. $C_{15}H_{22}O_2NCl$. Calculated %: N 4.94.

Removal of the ether from the neutral products by distillation gave 7.2 g of ω-bromoacetophenone.

1-Phenacyl-2,5-dimethyl-4-piperidinol Acetate (XXI, R= CH_3). For reaction was taken 1.5 g of 1-phenacyl-2,5-dimethyl-4-piperidinol (XIX) hydrochloride (m. p. 105-107°) and 7.5 ml of acetyl chloride, previously saturated with dry hydrogen chloride. The piperidinol (XIX) precipitate dissolved immediately. The mixture was let stand overnight. The next day the mixture was heated on the water bath for 1.5 hours. After cooling, dry hydrogen chloride was again passed through the solution. Removal of the solvent under slight vacuum gave a precipitate of the substance (1.7 g). After 2-fold precipitation with absolute ether from absolute alcohol and drying in a vacuum-desiccator the hydrochloride of 1-phenacyl-2,5-dimethyl-4-piperidinol acetate (XXI, R= CH_3) melted at 164-165°. Completely stable colorless crystals, soluble in water.

Found %: C 62.50, 62.36; H 7.36, 7.41; N 4.43, 4.45. $C_{17}H_{24}O_3NCl$. Calculated %: C 62.66; H 7.38; N 4.30.

1-Phenacyl-2,5-dimethyl-4-piperidinol Propionate (XXI, R= C_2H_5). For reaction 4.2 g of 1-phenacyl-2,5-dimethyl-4-piperidinol (XIX) hydrochloride (m. p. 105-107°) was mixed with 21 g of propionyl chloride (b. p. 78-79°), previously saturated with dry hydrogen chloride; here gas bubbles were evolved, and the solution turned dark and became homogeneous. The mixture was heated for 5 hours at 60-80°. The rest of the reaction was run the same as described in the preceding experiment.

After precipitation with absolute ether from anhydrous alcohol and drying in a vacuum-desiccator there was obtained 4.1 g of 1-phenacyl-2,5-dimethyl-4-piperidinol propionate (XXI, R= C_2H_5) hydrochloride, which melted at 171-173°. Colorless crystals, soluble in water.

Found %: C 63.6, 63.9; H 7.82, 7.85; N 4.17, 4.42. $C_{18}H_{26}O_3NCl$. Calculated %: C 63.78; H 7.73; N 4.13.

1-Phenacyl-2,5-dimethyl-4-piperidinol Benzoate (XXI, R= C_6H_5). For reaction was taken 1.6 g of 1-phenacyl-2,5-dimethyl-4-piperidinol (XIX) hydrochloride (m. p. 105-107°) and 7 ml of freshly-distilled benzoyl chloride, previously saturated with dry hydrogen chloride. The mixture was heated for 3 hours at 100-105°. For the remainder, the reaction was run the same as described above. The yield of substance was 2 g.

After precipitation with absolute ether from warm anhydrous alcohol the colorless crystals of the 1-phenacyl-2,5-dimethyl-4-piperidinol benzoate (XXI, R= C_6H_5) hydrochloride melted at 191.5-193°. The substance is soluble in water.

Found %: C 68.05 67.85; H 6.78, 6.51; N 3.76, 3.80. $C_{22}H_{26}O_3NCl$. Calculated %: C 68.11; H 6.75; N 3.65.

1-(2'-Hydroxy-2'-phenylpropyl)-2,5-dimethyl-4-piperidone (XXIV). The bromohydrin of the methyl phenyl glycol (XXII) was prepared essentially by the Tiffeneau method [9] from bromoacetone and phenylmagnesium bromide. In a nitrogen stream the methyl phenyl glycol bromohydrin (XXII) distilled at 105-107° (1 mm).

A mixture of 10.5 g of 2,5-dimethyl-4-piperidone (I) (b. p. 59-61° (5 mm)) and 8.81 g of freshly-distilled methyl phenyl glycol bromohydrin (XXII) in 40 ml of absolute ether was prepared. After 40 minutes a precipitate of the 2,5-dimethyl-4-piperidone hydrobromide began to separate. The next day the mixture was heated on the water bath for 3 hours. The precipitate was filtered and washed with dry ether (5 g). The ether was distilled off, the residue was treated with 20 ml of hydrochloric acid (1:1), and the neutral products were extracted twice with ether. The water layer was saturated with solid sodium hydroxide, and the oil separating here was extracted with five portions of ether. The ether extracts were dried over sodium sulfate. After distilling off the ether and 2,5-dimethyl-4-piperidone (2.1 g; b. p. 67-68° (6 mm)) the remaining colored oil was dissolved in dry ether, through which dry

hydrogen chloride was passed. At first the hydrochloride separated as a dark precipitate, the ether was decanted from it, and again hydrogen chloride was passed. The resulting precipitate was lighter in color. This operation was repeated 3 times.

After 3 recrystallizations from acetone the 1-(2'-hydroxy-2'-phenylpropyl)-2,5-dimethyl-4-piperidone (XXIV) hydrochloride obtained in this manner melted at 121-123°. Yield 2 g.

Found %: N 4.70, 4.96. $C_{16}H_{24}O_2NCl$. Calculated %: N 4.70.

SUMMARY

1. A number of 2,5-dimethyl-4-piperidone and 2,5-dimethyl-4-piperidinol derivatives were obtained, containing ketoalkyl radicals on the nitrogen. The synthesis of these derivatives was realized by the addition of α,β-unsaturated ketones, by the reaction with β-methoxyketones, and by the reaction with halo-substituted ketones.

2. A number of esters (acetates, propionates and benzoates) were synthesized by reacting the anhydrides and acid halides of the corresponding acids with the piperidinols (XVIII) and (XIX).

3. These esters (XX and XXI, R = CH_3, C_2H_5, C_6H_5) were subjected to pharmacological study, but failed to show appreciable activity (pain-killing, anesthetic and spasmolytic).

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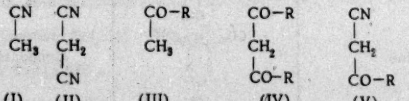
SYNTHESES AND TRANSFORMATIONS OF PYRIMIDINE DERIVATIVES

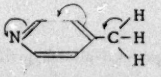
VII. RESPECTIVE INFLUENCE OF THE PYRIMIDINE AND PYRIDINE RINGS ON THE METHYL GROUP FOUND IN POSITION 4

N. V. Khromov-Borisov

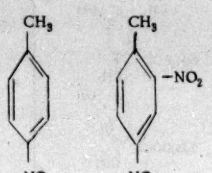
The accumulation of activator-groups in the molecule, exerting a favorable influence on either the methylene or methyl groups, increases the mobility of the hydrogen atoms in this group. This is well known on the examples of such compounds as (I-VIII), in which the activator-groups are CO−R; C ≡ N; NO_2:



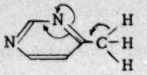
(I) (II) (III) (IV) (V)



(IX)



(VI) (VII) (VIII)



(X)

In a whole series of studies, especially those of A. E. Porai-Koshits and his school [1], it was shown that the nitrogen atom, present as a hetero atom in different hetero rings, exerts an activating influence on the methyl group provided it is found in conjugation with it.

In examining the chemical structure of compounds of the type of 4-methylpyridine (IX) and, correspondingly, of the type of 4-methylpyrimidine (X), the question arises: will the methyl group of the (X), type suffer noticeably greater activation under the influence of two hetero atoms than does the methyl group in compounds of the type of (IX) under the influence of only one hetero atom.

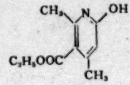
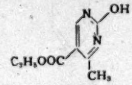
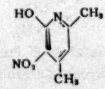
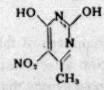
In order to answer this question we made a comparative study of the reaction ability of a number of 4-methylpyridine and 4-methylpyrimidine derivatives for condensation with aldehydes and diazo compounds. First of all we subjected 4-methylpyridine and 4-methylpyrimidine to such a study, failing to contain, other than methyl, any other substituents, and then we studied the more complex compounds, containing in positions 2, 5 and 6 the substituents CH_3, OH, $COOC_2H_5$ and NO_2. The activity of the methyl groups was compared for either completely analogous pyridine and pyrimidine derivatives (in the first two cases), or for compounds that were extremely close to each other in both the character and position of the substituents in the heterocyclic ring (in the last two cases).

Some data on the capacity of pyridine and pyrimidine compounds for condensation reactions on the basis of active methyl groups are known from the journal literature, while other data were obtained on the basis of our experimental work, described in previous communications [2-9].

The aldehydes used were benzaldehyde and p-dimethylaminobenzaldehyde, while the diazo compound used was p-nitrodiazobenzene. The results that we obtained are given in the table.

A comparison of the data given in the table (too be sure, still not very abundant) clearly shows that the methyl groups found in the 4 position of the pyrimidine nucleus, are more active than the methyl groups that are found in the 4 position of the pyridine nucleus.

As a result, it must be assumed that in the investigated pyrimidine derivatives the activating influence shown by two hetero atoms on one methyl group is cumulative (additive), since each of the hetero atoms is found in conjugation with it (the methyl group).

Name of Compound	Structural Formula	Degree of Activity of the Methyl Group
4-Methylpyridine		Condenses with aldehydes [2]; fails to couple with diazo compounds [3]
4-Methylpyrimidine		Condenses with aldehydes [4]; couples with diazo compounds [9]
2-Hydroxy-4,6-dimethylpyridine		Fails to condense with aldehydes [9]
2-Hydroxy-4,6-dimethylpyrimidine		Condenses with aldehydes [5, 6].
2-Hydroxy-4,6-dimethyl-5-carbethoxypyridine		Fails to condense with aldehydes [9]
2-Hydroxy-4-methyl-5-carbethoxypyrimidine		Condenses with aldehydes [7]
2,4-Dimethyl-5-nitro-6-hydroxypyridine		Condenses with aldehydes; fails to couple with diazo compounds [9]
2,6-Dihydroxy-5-nitro-4-methylpyrimidine		Condenses with aldehydes; couples diazo compounds [8]

If the reactivity of methylpyridine, methylpyrimidine and the nitrate toluenes is compared, then it is shown that the hetero N atom activates the methyl group to a greater degree than does the nitro group. Actually, methylpyridine (IX) condenses with aldehydes and nitroso compounds, while the nitrotoluene (VI) fails to condense with these compounds; methylpyrimidine (X) couples with diazo compounds, but the dinitrotoluene (VII) fails to couple. Only for the trinitrotoluene (VIII) is the ability for azo-coupling shown; consequently, on the basis of their influence on the methyl group the three nitro groups are approximately equal to two hetero N atoms. To a certain degree this relationship is also confirmed for the pyridine nucleus: the methyl groups in α- and γ-methylpyridines are more active than they are in the o- and p-mononitrotoluene (based on the reactions with aldehydes), but they are less active than the methyl groups in the 2,4- and 2,6-dinitrotoluenes (based on the reactions with nitroso compounds).

Consequently, as a very gross approximation it can be assumed that in its activating influence on the methyl group each hetero N atom (found in pyridines and pyrimidines) is roughly 1.5 times as powerful as the nitro group (found in nitrotoluenes).

SUMMARY

1. A comparative study was made of the activity of the methyl groups found in the 4-positions of the pyridine and pyrimidine rings, respectively. For this the studied pyridine and pyrimidine compounds were subjected to reaction with benzaldehyde, p-dimethylaminobenzaldehyde and p-nitrodiazobenzene.

2. In all of the studied cases the methyl group, found in the 4 position of the pyrimidine ring, proved to be more active than the methyl group (that was) found in the 4 position of the pyridine ring.

3. In the investigated pyrimidine compounds the activating influence shown by the two hetero N atoms proves to be additive, which is expressed in a higher activity for the methyl group found in the 4 position.

4. In its influence on the methyl group the degree of activation shown by each hetero N atom (found in pyridines and pyrimidines) is 1.5 times that shown by each nitro group (found in nitrotoluenes).

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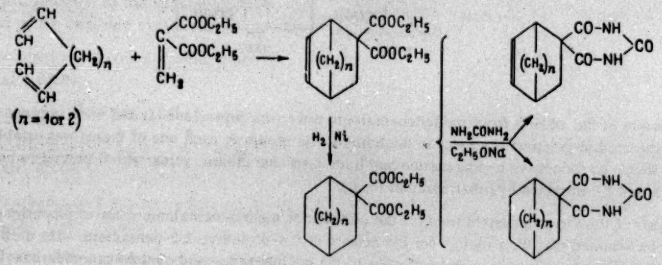
BARBITURIC ACIDS

IV. SYNTHESIS OF "SPIROBARBITURIC" ACIDS

R. Ya. Levina, N. N. Godovikov and F. K. Velichko

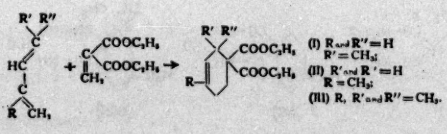
In the previous communication [1] we described the synthesis of "spirobarbituric" acids, based on the reaction of methylenemalonic ester with cyclopentadiene and cyclohexadiene:



These reactions gave unsaturated and saturated "spirobarbituric" acids, having in the carbocyclic radical either the endomethylene or endoethylene bridge.

In this paper we studied the reaction between methylenemalonic ester and the diene hydrocarbons with open-chain carbon atoms, namely, with piperylene (1,3-pentadiene), isoprene and 2,4-dimethyl-1,3-pentadiene.

Under the usual conditions of the diene synthesis we obtained: 1,1-dicarbethoxy-2-methyl-3-cyclohexene (I), 1,1-dicarbethoxy-4-methyl-3-cyclohexene (II) and 1,1-dicarbethoxy-2,2,4-trimethyl-3-cyclohexene (III) in respective yields of 25, 27 and 24%, based on methylenemalonic ester taken for reaction:

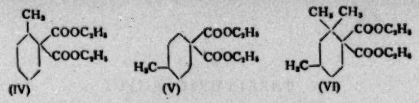


(I) R and R'' = H, R' = CH_3;
(II) R' and R' = H, R = CH_3;
(III) R, R' and R'' = CH_3.

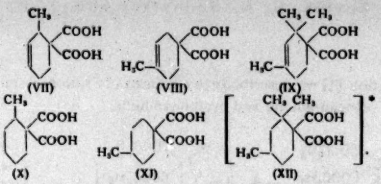
As a result, it was found that the "diene synthesis" reaction between methylenemalonic ester, functioning as a dienophile, and alkadienes of diverse structure is always realized under the same conditions and leads to the formation of adducts in practically the same, but low, yields.

It is known that a strong dienophile like maleic anhydride reacts with piperylene with greater difficulty than it does with isoprene [2, 3], while with 2,4-dimethyl-1,3-pentadiene it fails to react at all [4]. Consequently, it can be concluded that methylenemalonic ester is a stronger dienophile than maleic anhydride; the comparatively low yields of the adducts are due, apparently, to the considerable tendency shown by the methylenemalonic ester for polymerization.

The cyclohexenedicarboxylic acid esters synthesized by us were converted by hydrogenation into the corresponding cyclohexanedicarboxylic acid esters: 1,1-dicarbethoxy-2-methylcyclohexane (IV), 1,1-dicarbethoxy-4-methylcyclohexane (V) and 1,1-dicarbethoxy-2,2,4-trimethylcyclohexane (VI).

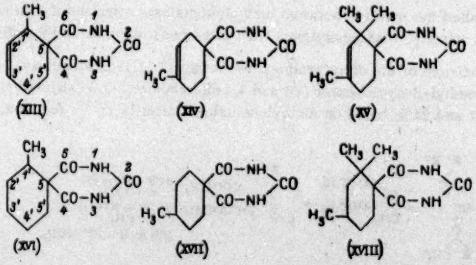


All of the unsaturated and saturated esters were identified by their conversion into the crystalline dibasic acids:



The structure of the adducts from methylenemalonic ester with piperylene (I) and with isoprene (II) (i.e. the position of the methyl group with respect to the carbethoxyl groups in each one of them) was established by obtaining from them, by successive hydrogenation and hydrolysis, the dibasic acids, which proved to be identical with the acids X and XI, obtained by other methods [5, 6].

On the basis of the direction established for the addition of methylenemalonic ester to piperylene and to isoprene it can be assumed that the structure for the adduct of 2,4-dimethyl-1,3-pentadiene with methylenemalonic ester corresponds to formula (III). The obtained esters of the cyclohexene- and cyclohexanedicarboxylic acids, being disubstituted malonic esters, were converted by treatment with urea in the presence of sodium ethylate into barbituric acids with the spirane structure:



Of the dibasic acids synthesized in the present study, their esters and the barbituric acids corresponding to the latter, the compounds that have been described in the literature are (II), (IV), (X), (XI) and (XVI).

EXPERIMENTAL

The piperylene (b. p. 40.4° at 749 mm, n_D^{20} 1.4308), isoprene (b. p. 32° at 749 mm, n_D^{20} 1.4217) and 2,4-dimethyl-1,3-pentadiene [7] (b. p. 91-92° at 749 mm, n_D^{20} 1.4446) were reacted with methylenemalonic ester** under the conditions described earlier [1]. Below we give the constants, yields and analysis data for the cyclohexenedicarboxylic acid esters that were prepared by us.

* The hydrolysis of 1,1-dicarbethoxy-2,2,4-trimethylcyclohexane (VI) gave the oily acid (XII), which we were unable to crystallize.

** The preparation of methylenemalonic ester is described in the previous communication [1].

1,1-Dicarbethoxy-2-methyl-3-cyclohexene (I; yield 25%): B. p. 133-134° (9 mm), n_D^{20} 1.4572, d_4^{20} 1.0456, MR_D 61.61. $C_{13}H_{20}O_4F$. Calc. 62.87.

Found %: C 63.92, 63.93; H 8.38, 8.44. $C_{13}H_{20}O_4$. Calculated %: C 63.49; H 8.34.

1,1-Dicarbethoxy-4-methyl-3-cyclohexene (II; yield 27%): B. p. 113-115° (4 mm), n_D^{20} 1.4532, d_4^{20} 1.0370; MR_D 63.06. $C_{13}H_{20}O_4F$. Calc. 62.87.

Literature [8]: B. p. 127° (6 mm), n_D^{25} 1.452, d_4^{25} 1.030.

1,1-Dicarbethoxy-2,2,4-trimethyl-3-cyclohexene (III; yield 24%): B. p. 119-121° (4 mm), n_D^{20} 1.4632, d_4^{20} 1.0266, MR_D 72.04. $C_{15}H_{24}O_4F$. Calc. 72.11.

Found %: C 67.01; 66.95; H 8.94, 8.95. $C_{15}H_{24}O_4$. Calculated %: C 67.13; H 9.02.

The hydrogenation of the adducts was run in the cold in anhydrous alcohol, in the presence of skeletal nickel. The constants of the obtained cyclohexanedicarboxylic acid esters are given below.

1,1-Dicarbethoxy-2-methylcyclohexane (IV): B. p. 120-121 (7 mm), n_D^{20} 1.4490, d_4^{20} 1.0345, MR_D 62.82. $C_{13}H_{22}O_4$. Calc. 63.34.

Literature [5]: B. p. 131-133° (11 mm).

1,1-Dicarbethoxy-4-methylcyclohexane (V): B. p. 125-127° (8 mm), n_D^{20} 1.4458, d_4^{20} 1.0154, MR_D 63.76. $C_{13}H_{22}O_4$. Calc. 63.34.

1,1-Dicarbethoxy-2,2,4-trimethylcyclohexane (VI): B. p. 141-143° (11 mm), n_D^{32} 1.4584, d_4^{20} 1.0162, MR_D 72.69. $C_{15}H_{26}O_4$. Calc. 72.58.

Hydrolysis. The cyclohexene- and cyclohexanedicarboxylic acid esters were hydrolyzed by treatment with alcoholic potassium hydroxide solution as described by us earlier [1]. The melting points, yields and analysis data for the obtained dicarboxylic acids are shown in Table 1.

TABLE 1

Yields and Analysis Data for the Dicarboxylic Acids

Name	Melting Point	Yield (in %)	Found (%)		Calculated (%)	
			C	H	C	H
1,1-Dicarboxy-2-methyl-3-cyclohexene (VII)	121-122°	56	58.92, 58.69	6.75, 6.75	58.68	6.57
1,1-Dicarboxy-4-methyl-3-cyclohexene (VIII)	163-164 (with decomp.)	53	58.74, 58.74	6.62, 6.65	58.68	6.57
1,1-Dicarboxy-2,2,4-trimethyl-3-cyclohexene (IX)	194-195 (with decomp.)	35	62.09, 61.94	7.85, 7.84	62.26	7.59
1,1-Dicarboxy-2-methylcyclohexane • (X)	154-155	98	57.69, 57.75	7.60, 7.63	58.09	7.57
1,1-Dicarboxy-4-methylcyclohexane•• (XI)	175-176	98	58.30, 58.23	7.68, 7.55	58.09	7.57

• Literature [5]: M. p. 154-155°.

•• Literature [6]: M. p. 175°.

Spirobarbituric Acids. Urea (4 g, 0.07 mole) was added to the sodium alcoholate (0.7 g in 20 ml of anhydrous alcohol), and then the proper saturated or unsaturated ester (0.01 mole). The reaction mixture was heated in an oil bath at 100-110° for 6 hours. The alcohol-insoluble sodium salt of the barbituric acid obtained here as a precipitate was filtered,• washed with alcohol, then with ether, and finally dried in the air. Acidification of the product with dilute hydrochloric acid gave the spirobarbituric acid, which was then recrystallized from dilute alcohol. The melting points, yields and analysis data for the obtained spirobarbituric acids are given in Table 2.

• In some cases the filtrate was evaporated nearly to dryness and an additional amount of the barbituric acid was isolated from the residue by treating it with dilute hydrochloric acid.

TABLE 2

Spirobarbituric Acids (Cyclohexene- and Cyclohexane-gem-dicarboxylic Acid Ureides)

Name	Melting point	Yield (in %)	Nitrogen Content (in %)	
			Found	Calculated
1,1-Dicarboxy-2-methyl-3-cyclohexene ureide (XIII)	220-221°	26	13.52, 13.45	13.45
1,1-Dicarboxy-4-methyl-3-cyclohexene ureide (XIV)	223-224 (with decompn.)	53	13.80, 13.71	13.45
1,1-Dicarboxy-2,2,4-trimethyl-3-cyclohexene ureide (XV)	Decomposes at 229-230°	17	12.04, 12.01	11.85
1,1-Dicarboxy-2-methylcyclohexane ureide (XVI)	217-218 (with decompn.)*	25	13.68, 13.40	13.32
1,1-Dicarboxy-4-methylcyclohexane ureide (XVII)	251-252	66	13.87, 13.68	13.32
1,1-Dicarboxy-2,2,4-trimethylcyclohexane ureide (XVIII)	217-218 (with decompn.)	24	12.14, 12.04	11.76

* Literature [9]: M. p. 219.5-220°.

SUMMARY

1. The "diene synthesis" between methylenemalonic ester as the dienophile and the alkadienes piperylene, isoprene and 2,4-dimethyl-1,3-pentadiene was accomplished.

2. It was established that these reaction products have the structure of 1,1-dicarbethoxy-2-methyl-3-cyclohexene, 1,1-dicarbethoxy-4-methyl-3-cyclohexene and 1,1-dicarbethoxy-2,2,4-trimethyl-3-cyclohexene, respectively.

3. The obtained cyclohexenedicarboxylic acid esters were converted by hydrogenation into the corresponding saturated esters – 1,1-dicarbethoxy-2-methylcyclohexane, 1,1-dicarbethoxy-4-methylcyclohexane and 1,1-dicarbethoxy-2,2,4-trimethylcyclohexane.

4. All of the esters (identified by their conversion into crystalline dibasic acids) synthesized by us were converted by treatment with urea in the presence of sodium ethylate into spirobarbituric acids.

5. Some previously unknown cyclohexene- and cyclohexane-gem-dicarboxylic esters and the gem-dicarboxylic acids and spirobarbituric acids corresponding to them are described.

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CATALYTIC TRANSFORMATIONS OF ETHYLENE SULFIDE AND ETHANEDITHIOL

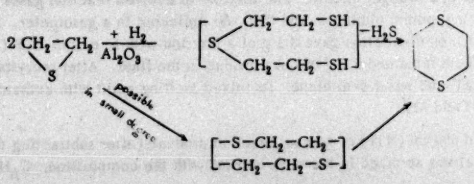
Yu. K. Yuryev and L. S. German

Earlier it was shown by one of us that ethylene oxide in contact with aluminum oxide at 200° is not only partially isomerized into acetaldehyde [1], but also suffers dimerization with the formation of 1,4-dioxane [2].

The reaction of ethylene oxide with hydrogen sulfide under the same conditions gives 1,4-dioxane, 1,4-dithiane and 1,4-thioxane. At higher temperature the ethylene oxide reacts with hydrogen sulfide in a different manner. Already at 300° the formation of thiophene is observed, the yield of which increases with temperature elevation and at 450° reaches 5.3%. The formation of thiophene under these more drastic conditions is due to the reaction of hydrogen sulfide with the acetaldehyde that appears as the product of ethylene oxide isomerization. Ethylene glycol behaves in a similar manner under the indicated conditions [3-5].

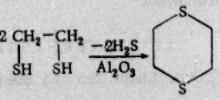
In connection with this it appeared of interest to study under the same conditions the behavior of ethylene sulfide and ethanedithiol, being the sulfur analogs of ethylene oxide and ethylene glycol, respectively. In this study it was established that ethylene sulfide, in contact with aluminum oxide at 220° in the absence of hydrogen sulfide, suffers dimerization with the formation of 1,4-dithiane in 41% yield, which is accompanied by considerable substance decomposition with the evolution of hydrogen sulfide. When in contact with aluminum oxide under the same temperature conditions, but in a hydrogen sulfide atmosphere, the ethylene sulfide is almost quantitatively converted into 1,4-dithiane.

It is postulated that the most probable course for the last reaction is the intermediate formation of β,β-dimercaptodiethyl sulfide as the result of hydrogen sulfide addition to ethylene sulfide. This intermediate product, cleaving hydrogen sulfide, gives 1,4-dithiane.*



The absence in the catalyzates of thioparaldehyde, the stable form of thioacetaldehyde, and also the absence of thiophene in the catalyzates obtained at 350 and 400°, indicates that ethylene sulfide fails to suffer isomerization into thioacetaldehyde under the conditions that are favorable for the isomerization of ethylene oxide into acetaldehyde (contact with aluminum oxide, elevated temperature).

1,2-Ethanedithiol failed to suffer change when brought in contact with aluminum oxide at 220° in a nitrogen atmosphere; at a higher temperature (300°) the 1,2-ethanedithiol was converted into 1,4-dithiane (in 51% yield):



Further elevation of the temperature to 380° only caused profound decomposition of the 1,2-ethanedithiol.

As for the ethylene sulfide neither thioparaldehyde nor thiophene could be found in the catalyzates that were obtained from the contact reaction of 1,2-ethanedithiol with aluminum oxide.

* According to the literature [6]. β,β-dimecarptodiethyl sulfide cleaves hydrogen sulfide with the formation of 1,4-dithiane.

EXPERIMENTAL

The ethylene sulfide (b. p. 54-56° at 760 mm) was obtained by the G. I. Braz method [7].

Behavior of Ethylene Sulfide in Contact with Aluminum Oxide

1) Ten grams (0.16 mole) of ethylene sulfide was passed at a rate of 8-10 drops a minute in a nitrogen stream through a tube filled with aluminum oxide (internal diameter of the tube 10 mm, length of catalyst layer 40 cm) and heated to 220°. After passing through a wash bottle containing sodium plumbite the gases evolved from the reaction were collected in a gasometer. After all of the ethylene sulfide had been added the temperature was raised to 260°, and nitrogen was passed through for another 30 minutes to displace any reaction products. In the receiver was collected 4.1 g (41%) of catalyzate – crystals with m. p. 110-111° (from ether), being 1,4-dithiane. The mixed melting point of these crystals with authentic 1,4-dithiane failed to be depressed; m. p. 110°.

Literature for 1,4-dithiane [8]: m. p. 111-112°.

In the gasometer was collected 700 ml (NTP) of gaseous reaction products (after subtracting the introduced nitrogen and the hydrogen sulfide that was absorbed in the wash bottles) with the composition: C_nH_{2n} 66%, H_2 33%. Passage of the gas through a wash bottle containing bromine gave dibromoethane with b. p. 131-133° and n_D^{20} 1.5350.

2) 220°. Ten grams (0.16 mole) of ethylene sulfide was passed over aluminum oxide at a rate of 8-10 drops a minute in a stream of hydrogen sulfide. The yield of catalyzate was 9.4 g (94%), being 1,4-dithiane; m. p. 110.5°. Its mixed melting point with authentic 1,4-dithiane failed to be depressed.

3) 300°. From 10 g of ethylene sulfide, passed over aluminum oxide in a hydrogen sulfide stream, was obtained 3.9 g (39%) of 1,4-dithiane with m. p. 110°. Its mixed melting point with authentic 1,4-dithiane failed to be depressed.

4) 350°. From 10 g of ethylene sulfide, passed over aluminum oxide in a hydrogen sulfide stream, was obtained 0.24 g (2.4%) of 1,4-dithiane, m. p. 110°. Its mixed melting point with authentic 1,4-dithiane failed to be depressed.

Behavior of 1,2-Ethanedithiol in Contact with Aluminum Oxide

Ten grams (0.1 mole) of 1,2-ethanedithiol (b. p. 145-146° at 758 mm; n_D^{20} 1.5579) was passed over aluminum oxide at a rate of 5-6 drops a minute in a nitrogen stream. The mixture of evolved reaction gases and nitrogen was passed through a wash bottle containing sodium plumbite, and then was collected in a gasometer. In the receiver was collected 4 g of catalyzate, which on distillation gave 3.1 g of a fraction with b. p. 185-210° (751 mm), becoming crystalline on cooling. There remained 0.8 g of tarry residue in the flask. After recrystallization from ether the substance melted at 110-111° and was 1,4-dithiane. Its mixed melting point with authentic dithiane failed to be depressed; m. p. 110°. Yield 51%.

In the gasometer was collected 600 ml (NTP) of gaseous reaction products (after subtracting the introduced nitrogen and the hydrogen sulfide that was absorbed in the wash bottles) with the composition: C_nH_{2n}, 66%, H_2 17.3%, C_nH_{2n+2} 16.6%.

SUMMARY

1. When in contact with aluminum oxide at 220°, both in the absence and in the presence of hydrogen sulfide, ethylene sulfide yields 1,4-dithiane.

2. 1,2-Ethanedithiol in contact with aluminum oxide at 300° yields 1,4-dithiane. At 220° the ethanedithiol fails to be changed while at 380° it is decomposed.

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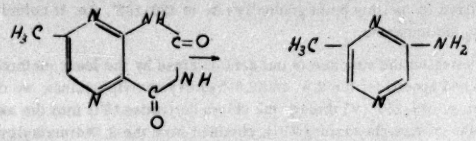
STRUCTURE OF THE PYRAZINE DERIVATIVES OBTAINED BY THE CONDENSATION OF AMINOMALONODIAMIDE WITH METHYLGLYOXAL

T. V. Gortinskaya and M. N. Shchukina

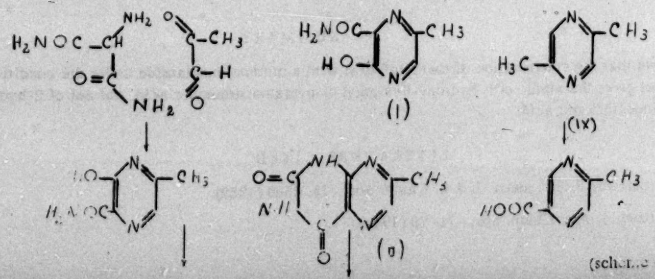
As starting substance for synthetic work in the field of pyrazine derivatives we found it necessary to have 2-hydroxy-5-methylpyrazine. This compound was obtained by Karmas and Spoerri [1] in 27% yield by the condensation of glycinamide hydrochloride with methylglyoxal, together with an 8% yield of the 2,6-isomer. The present work continues the studies of Jones [2], who proposed a new synthesis method for hydroxypyrazines via the condensation of 1,2-dicarbonyl compounds with the amides of α-amino acids. When this reaction was applied to unsymmetrical dicarbonyl compounds Jones obtained exclusively the 2,5-dialkyl- or the arylhydroxypyrazines in good yields. Karmas changed the reaction conditions, using the hydrochlorides instead of the difficulty available free bases of the α-amino acid amides and obtained in a number of cases the 2,6-isomers or a mixture of the 2,6- and 2,5-isomers.

The structure of the hydroxymethylpyrazines obtained by Karmas was established by him on the basis of comparing the aminomethylpyrazines that were obtained from the corresponding hydroxy compounds through the chloro derivatives with the 2-amino-6-methylpyrazine that was obtained from methyllumazine, the structure of which fails to evoke any doubt [3].



On the basis of these data we selected for obtaining the 2-hydroxy-5-methylpyrazine the reaction described by Jones and specifically the condensation of methylglyoxal with aminomalonodiamide, in contrast to Karmas, who used the hydrochloride of aminoglycinamide. In this reaction we should have obtained the amide of 2-hydroxy-5-methylpyrazinecarboxylic acid (I). This amide was obtained by Jones and after saponification gave the acid with m. p. 155-157°. To prove the structure of the acid obtained by him Jones compared it with the 2-hydroxy-6-methyl-3-pyrazinecarboxylic acid (IV) that was obtained from the lumazine (II) through the 2-amino-6-methyl-3-pyrazinecarboxylic acid (III), the structure of which was shown earlier.

The 2-hydroxy-6-methyl-3-pyrazinecarboxylic acid (IV) that was obtained from the lumazine has m.p. 182-183°. Its mixed melting point with the acid obtained by Jones was 150-155°. Jones accepted these facts as sufficient proof that the acid obtained by him was different from the acid obtained from the lumazine and that, consequently, his acid was 2-hydroxy-5-methyl-3-pyrazinecarboxylic acid.



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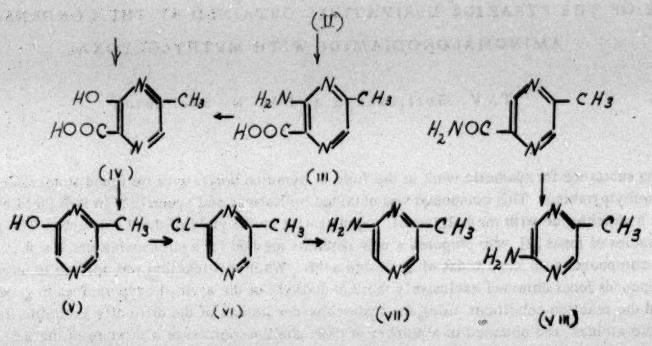

We repeated the work of Jones, hoping to obtain 2-hydroxy-5-methylpyrazine in the decarboxylation of this acid, but instead the free base isolated by us in 60% yield had m. p. 249-250°, and not the 126-128° indicated by Karmas for the 2,5-isomer, which, consequently, indicated that it was the 2,6-isomer (Karmas gives for it a m. p. of 250-251°). From this it can be concluded that the acid obtained by Jones was identical with the acid obtained from the lumazine, but insufficiently pure. Actually, when the acid obtained by us by the Jones method, with m. p. 156-157°, was repeatedly recrystallized its melting point gradually rose to 180-182°, i.e. it coincided with the melting point of the acid obtained from the lumazine.

In order to conclusively establish the structure of our acid obtained by the Jones method, and also to verify the constants given by Karmas and Spoerri for the 2,5- and 2,6-hydroxymethylpyrazines, we decided to convert the hydroxymethylpyrazine with m. p. 249-250° (V) through the chloro derivative (VI) into the aminomethylpyrazine (VII) and compare it with the 2-amino-5-methylpyrazine (VIII), obtained from the 2,5-dimethylpyrazine [3, 4].

As a result, it can be confidently stated that the amide and acid (characterized by Jones as being 2-hydroxy-3-carboxy (amide)-5-methylpyrazine) is actually the 2-hydroxy-3-carboxy(amide)-6-methylpyrazine, and that running the reaction under his conditions gives mainly the 2,6-derivative.

EXPERIMENTAL

Decarboxylation of 2-Hydroxy-3-carboxy-6-methylpyrazine. A mixture of 6 g of 2-hydroxy-3-carboxy-6-methylpyrazine with 45 ml of nitrobenzene was heated until the substance dissolved. After cooking with activated carbon the solution was filtered, and the crystals obtained after cooling were separated and washed well with ether. The yield of substance with m. p. 240-245° was 2.6 g (61%). Two recrystallizations from methyl alcohol gave snow-white plates with m. p. 249-250° and showing ready sublimation.

Found %: C 54.69; H 5.46. $C_6H_6ON_2$. Calculated %: C 54.53; H 5.45.

The other transformations were run by described methods.

SUMMARY

It was shown that the condensation of methylglyoxal with aminomalonodiamide under the conditions described by Jones gives the amide of 2-hydroxy-6-methyl-3-pyrazinecarboxylic acid, and not of 2-hydroxy-5-methyl-3-pyrazinecarboxylic acid.

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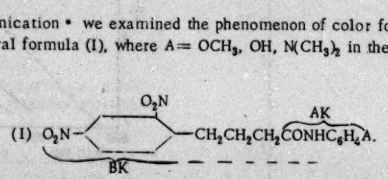
SEPARATED CHROMOPHORE SYSTEMS

XXXI. COMPARATIVE STUDY OF THE ABSORPTION SPECTRA FOR THE ARYLAMIDES OF 2,4-DINITROPHENYLACETIC, 2,4-DINITROHYDROCINNAMIC AND γ-(2,4-DINITROPHENYL)BUTYRIC ACIDS

E. A. Smirnov

In the previous communication * we examined the phenomenon of color for the arylamides of γ-(2,4-dinitrophenyl)butyric acids of general formula (I), where A = OCH_3, OH, $N(CH_3)_2$ in the meta or para-position with respect to the NH-group.



For the sake of comparison we also made a color study of the analogous 2,4-dinitrophenylacetic and 2,4-dinitrohydrocinnamic acid derivatives, which permitted us to observe a regularity in the color change when going from one series of compounds to another. The conclusions that we obtained here were made on the basis of visual observations and were confirmed by the reflection spectra of the substances, taken in the solid form.

In this communication we examine the absorption spectra of the above indicated series of compounds. The corresponding absorption curves are shown in Figs. 1-6. An examination of these curves draws attention first of all to the fact that the analogous curves of all three series of compounds are extremely close among themselves and especially in the short-wave region (in the upper portion of the curve). All of the curves are characterized by the presence of a well-defined maximum in the short-wave region, the position of which depends chiefly on the character and position of the electron-donor group and is very slightly dependent as to which of the three series of compounds the given curve belongs. The most bathochromic position of this maximum is found for the compounds with a p-$N(CH_3)_2$-group 270-272 mμ), and the most hypsochromic for the compounds with a m-$N(CH_3)_2$-group (237-272 mμ); its position is practically the same (250-252 mμ) for the compounds with p-OCH_3- and p-OH-groups, while for the compounds with m-OCH_3- and M-OH-groups it is shifted somewhat to the hypsochromic side when compared with the paraisomers (245-248 mμ). If the position of the maximum in the short-wave region for the dinitro derivatives is compared with the position of the maximum for the corresponding mononitro derivatives, described by us earlier, described by us earlier,** then in all cases it is shifted toward the hypsochromic side for the dinitro derivatives when compared with the maxima for the mononitroderivatives: by 6 mμ when the p-$N(CH_3)_2$-group is present, 6-10 mμ when either the p-OCH_3- or p-OH-group is present, 4-5 mμ when the m-OCH_3-group is present, and by 2 mμ when either the m-OH- or m-$N(CH_3)_2$-group is present.

The second, longer wavelength band, present for all of the examined compounds, appears as a well-defined step with a maximum, which can be determined only approximately: for the compounds with a $N(CH_3)_2$-group (irrespective of whether it is in the meta- or para-position) it is situated at ~350 mμ, while for all of the compounds with either a OCH_3- or OH-group it lies at ~330 mμ. This step is also present for the mononitro compounds, but for these it is expressed somewhat more weakly: its position is approximately the same as it is for the dinitro derivatives.

All of the compounds with an electron-donor group in the meta-position (Figs. 4, 5 and 6) have a third band situated between the first two and also appearing as a step, clearly defined for the compounds with a m-$N(CH_3)_2$-group. Its maximum is located at approximately 280 mμ. This band fails to be present for the compounds with a para-donor group. Finally it is necessary to consider the rise in the lower branch of the curves, which characterizes the absorption of light in the visible portion of the spectrum. This rise is different for analogous compounds of the different series: in the presence of the $N(CH_3)_2$-group it appears most strongly for the dinitrophenylacetic acid derivatives (Figs. 3 and 6), and in the presence of either the OCH_3- or OH-group it is strongest for the dinitro-

* J. Gen. Chem., 25, 2336 (1955) [Consultants Bureau Translation pagination 2309].

** J. Gen. Chem., 25, 1014 (1955) [Consultants Bureau Translation pagination 979].

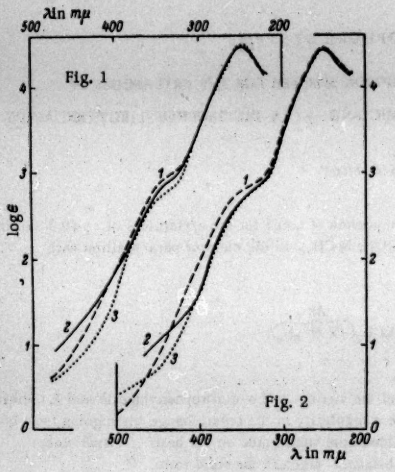


Fig. 1. See Figs. 1 and 2 for the meanings of DPA, DHC and DPB.
1) DPA-$NHC_6H_4OCH_3$-p, 2) DHC-$NHC_6H_4OCH_3$-p, 3) DPB-$NHC_6H_4OCH_3$-p.
Fig. 2. See Figs. 1 and 2 for the meanings of DPA, DHC and DPB.
1) DPA-NHC_6H_4OH-p, 2) DHC-NHC_6H_4OH-p, 3) DPB-NHC_6H_4OH-p.
DPA = 2,4-$(O_2N)_2C_6H_3CH_2CO$, DHC = 2,4-$(O_2N)_2C_6H_3(CH_2)_2CO$, DPB = 2,4-$(O_2N)_2C_6H_3(CH_2)_3CO$.

hydrocinnamic acid derivatives (Figs. 1, 2, 4 and 5), where for the compounds with a m-OCH_3-group it assumes the form of a very clearly defined step (Fig. 4, Curves 1 and 2). The presence of this rise on the curve can be regarded as being the result of intermolecular reaction between the electron-acceptor (BK) and electron-donor (AK) systems, contained in each of the molecules of formula (I), which, in our opinion, is the main factor in determining the color of the compounds examined by us. But if this reaction can appear in full measure for the substances in the solid state, then in solution it is disturbed to a considerable degree, in which connection this degree of disturbance is not the same for analogous compounds in the different series; consequently, the light-absorption curves in the given case do not permit judging as to the relative depth of color of corresponding compounds. Thus, for example, of the three curves, corresponding to the three analogous compounds with the p-$N(CH_3)_2$-group (Fig. 3), the most hypsochromic position is occupied by the curve for the dinitrophenylbutyric acid derivative, although in the solid state this compound

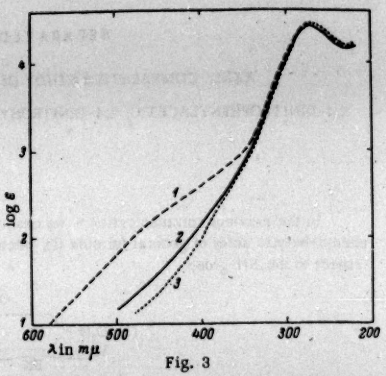


Fig. 3

1) DPA-$NHC_6H_4N(CH_3)_2$-p, 2) DHC-$NHC_6H_4N(CH_3)_2$-p, 3) DPB-$NHC_6H_4N(CH_3)_2$-p.
See Figs. 1 and 2 for the meanings of DPA, DHC and DPB.

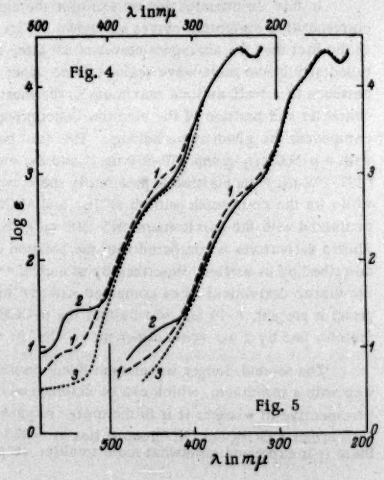


Fig. 4

1) DPA-$NHC_6H_4OCH_3$-m, 2) DHC-$NHC_6H_4OCH_3$-m, 3) DPB-$NHC_6H_4OCH_3$-m.

Fig. 5

1) DPA-NHC_6H_4OH-m, 2) DHC-NHC_6H_4OH-m, 3) DPB-NHC_6H_4OH-m.
The meanings of DPA, DHC and DPB are the same as in Figs. 1 and 2.

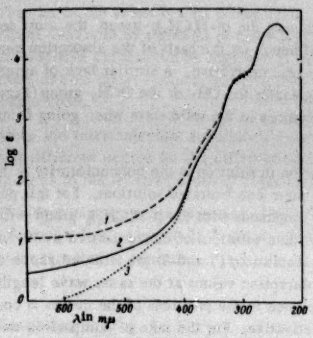


Fig. 6. 1) DPA-$NHC_6H_4N(CH_3)_2$-m; 2) DHC-$NHC_6H_4N(CH_3)_2$-m; 3) DPB-$NHC_6H_4N(CH_3)_2$-m.

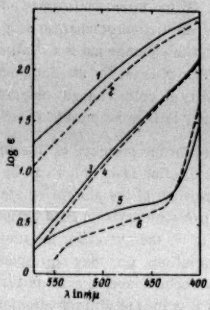


Fig. 7. DPA-$NHC_6H_4N(CH_3)_2$-p, $3 \cdot 10^{-2}$M; 2) Ditto $3 \cdot 10^{-3}$M; 3) DHC-$NHC_6H_4N(CH_3)_2$-p, $3 \cdot 10^{-2}$M; 4) Ditto $3 \cdot 10^{-3}$M; 5) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$ + $CH_3CONHC_6H_4N(CH_3)_2$, $3 \cdot 10^{-2}$M; 6) Ditto $3 \cdot 10^{-3}$M.

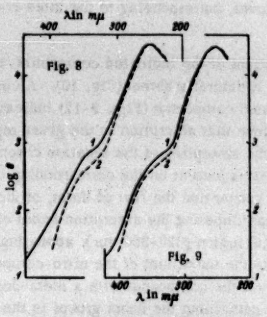


Fig. 8. 1) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONHC_6H_4OCH_3$-p; 2) sum of the absorption curves of 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$ + p-$CH_3CONHC_6H_4OCH_3$.

Fig. 9. 1) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONHC_6H_4OH$-p; 2) sum of the absorption curves of 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$ + p-$CH_3CONHC_6H_4OH$.

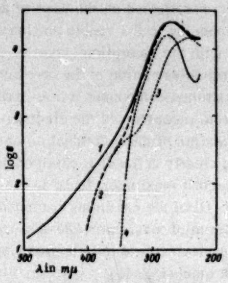


Fig. 10. 1) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH$ $C_6H_4N(CH_3)_2$-p; 2) sum of the absorption curves of 3 and 4, 3) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$, 4) p-$CH_3CONHC_6H_4N(CH_3)_2$.

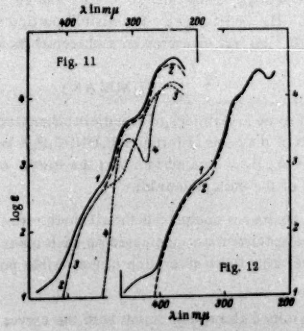


Fig. 11. 1) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONHC_6H_4N(CH_3)_2$-m; 2) sum of the absorption curves of 3 and 4; 3) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$. 4) m-$CH_3CONHC_6H_4N(CH_3)_2$.

Fig. 12. 1) 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONHC_6H_4OH$-m; 2) sum of the absorption curves 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$ + m-$CH_3CONHC_6H_4OH$.

has the deepest color. Of the three analogous compounds, containing the m-$N(CH_3)_2$-group, the most deeply colored in the solid state is the dinitrohydrocinnamic acid derivative, although on the basis of the absorption curves (Fig. 6) it might be thought that this compound is a dinitrophenylacetic acid derivative. A similar lack of agreement is also observed in a number of cases for the compounds containing either the OH- or the OCH_3-group (Figs. 1 and 2). As a result, the regularity in color change, observed for the substances in the solid state when going from one series of compounds to another, fails to be present in solution.

Also further proof for the presence of intermolecular reaction in solution is the nonconformity of the examined compounds to the Beer dilution law, which can be shown in the more concentrated solutions. For this purpose we measured the visible portions of the absorption spectra for two compounds with the p-$N(CH_3)_2$-group – the dinitrophenylacetic and dinitrohydrocinnamic acid derivatives – in pyridine solutions of concentration $3 \cdot 10^{-2}$ and $3 \cdot 10^{-3}$ mμ. As can be seen from Fig. 7, the curves for the more concentrated solutions (1 and 3) are situated above the curves for the less concentrated solutions, i.e. they correspond to greater absorption values at the same wave lengths, in which connection for the dinitrophenylacetic acid derivative this difference in the positions of the curves is considerably more pronounced than it is for the dinitrohydrocinnamic acid derivative. For the sake of comparison we show in the same figure the absorption curves for a mixture of two components, 2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$ and p-$CH_3CONHC_6H_4N(CH_3)_2$, in composition close to that of the electron-acceptor and electron-donor systems found in the examined compounds (Curves 5 and 6); and here also the curves, corresponding to the more concentrated solution (5), is situated above.

For the curves, constructed on the basis of adding the absorptions of the indicated compounds, the lower branch of the curve, corresponding to the visible portion of the spectrum, is naturally absent (Fig. 10). A comparison of the additive curves with the absorption curves of similarly constituted compounds (Figs. 8-12) indicates their great similarity in the ultraviolet portion of the spectrum. This is evidence that absorption in the given region of the spectrum for the examined compounds is essentially composed of the absorption of the separate chromophore systems – the electron-acceptor and the electron-donor. The maxima present on the corresponding curves correspond to the maxima of the individual components, in which connection the first of them, of shortest wavelength and the most clearly defined, is obtained as the result of superimposing the absorption bands of both components. The second maximum, found in the longer wavelength region (330-350 mμ), appearing only as a step and also present for all of the examined compounds, corresponds to the maximum of the nitro-components (Figs. 10 and 11). Finally, the third maximum (280-300 mμ), present only for the compounds with a meta-donor group, answer to the corresponding maximum of the electron-donor components, containing the donor groups in the meta-position with respect to each other (Fig. 11).

We used a Beckmann spectrophotometer for measuring the light-absorption spectra. The solvent used by us was purified alcohol, previously distilled through a fractionating column. The solution concentrations used for the spectral measurements were: $2 \cdot 10^{-3}$ and 10^{-4} M for the compounds with either the OH- or OCH_3-group; 10^{-3} and 10^{-4} M for the compounds with the $N(CH_3)_2$-group; and 10^{-2}, 10^{-3} and 10^{-4} for the separate components [2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$ and $CH_3CONHC_6H_4A$]. The visible portion of the spectrum in the more concentrated pyridine solutions ($3 \cdot 10^{-2}$ and $3 \cdot 10^{-3}$ M) was measured on a universal monochromator ("UM").

SUMMARY

1. The absorption spectra of some arylamides of 2,4-dinitrophenylacetic, 2,4-dinitrohydrocinnamic and γ-(2,4-dinitrophenyl)butyric acids of the general formula $RCONHC_6H_4A$ were measured, where A is one of the electron-donor groups – OH, OCH_3, $N(CH_3)_2$, located in either the meta- or para-position with respect to the NH-group, and RCO is the acyl radical of the indicated acids.

2. The absorption curves of analogous compounds for all three series are extremely close to each other, and in the ultraviolet portion of the spectrum are superposed on each other to a considerable degree. Only the lower branch of the curve, characterizing light-absorption in the visible portion of the spectrum, shows that they are slightly different.

3. The similarity of the examined absorption curves with the curves constructed on the basis of adding the absorptions of the two separate components [2,4-$(O_2N)_2C_6H_3CH_2CH_2CONH_2$ and $CH_3CONHC_6H_4A$], in their composition being close to that of the electron-acceptor and electron-donor systems found in the studied compounds, suggests that the absorption spectra of the latter are essentially composed of the absorptions of the individual systems.

4. The rise in the lower branch of the curve, corresponding to the absorption of light in the visible portion of the spectrum, observed to a greater or lesser degree for all of the studied compounds and at the same time absent in the additive curves, can be regarded as being the result of intermolecular reaction between the electron-acceptor and electron-donor systems, entering into the composition of these compounds, and this is the main reason for their visible color.

5. Since the intermolecular reaction is disturbed to considerable degree in dilute solutions and in this connection to different degree for the different compounds, then the absorption curves in the given case do not permit judging as to the relative depth of color for the compounds.

6. The deviation from the Beer law, which we were able to show for some of the examined compounds in more concentrated solutions ($3 \cdot 10^{-2}$ and $3 \cdot 10^{-3}$ M), can be regarded as also being evidence for the presence of intermolecular reaction in solution.

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Moscow Petroleum Institute

LETTERS TO THE EDITOR

In the paper "Mechanism of the Reaction of Formation of Oxazolones Substituted in the 2-Position", published in J. Gen. Chem. 23. 438 (1953) (T. p. 449)*, the anhydride of N-acetylphenaceturic acid with m. p. 175-176° was described. This should read as "2-benzylidene-3-acetyl-5-oxazolone", which was obtained by M. M. Shemyakin. S. I. Lurye and E. I. Rodionovskaya (J. Gen. Chem., 19, 769 (1949) (T. p. 749)*.

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I. T. Strukov

* T. p. = Consultants Bureau Translation pagination.